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REMOVAL OF FLUORIDES FROM WATER SUPPLIES

Alberta
ENVIRONMENT
Standards And Approvals Division
Municipal Engineering Branch

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REMOVAL OF FLUORIDES FROM WATER SUPPLIES

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Removal of Fluorides from Water Supplies

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Prepared for:

Alberta Environment
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ABSTRACT

Excessive concentrations of fluoride in drinking water have significant public health implications. The most common problem observed at relatively low levels (2 mg/L) is mottling of children's teeth. Higher levels increase the severity of this problem and also lead to other health problems in both adults and children.

There are basically three types of treatment methods for fluoride removal. The additive methods rely on adding chemicals to the water during the coagulation or softening processes to remove fluorides with the resulting flocs. Another type of treatment is based upon an ion exchange or adsorption process in contact columns. The fluoride ion can also be removed in demineralization processes, such as reverse osmosis and electrodialysis, but these processes are not designed strictly for fluoride removal.

Common chemicals used in the additive methods are alum, lime and magnesium compounds. Large doses are required to achieve significant fluoride removal. These methods are limited to relatively low fluoride levels and to certain specific conditions. Bone materials and activated alumina, when used in contact beds, can effectively reduce fluoride to very low levels. Moreover, they can be regenerated. Activated alumina defluoridation seems to be most accepted technology for fluoride removal in full-scale operations.

Table of Contents

Chapter Page

1. INTRODUCTION 1
2. NEEDS FOR FLUORIDE REMOVAL 3
   - 2.1 HEALTH CONSIDERATIONS 3
     - 2.1.1 Fluoride in Human Body 3
     - 2.1.2 Dental Effects 4
     - 2.1.3 Skeletal Fluorosis 5
     - 2.1.4 Kidney-related Problems 6
     - 2.1.5 Effects on Enzymes 7
     - 2.1.6 Other Implications 8
   - 2.2 WATER USERS AFFECTED BY FLUORIDES IN THE WATER 9
   - 2.3 OPTIMUM AND PERMISSIBLE LEVELS OF FLUORIDE 9
   - 2.4 FLUORIDE LEVELS IN ALBERTA 11
3. FLUORIDE REMOVAL TECHNOLOGIES 22
   - 3.1 ADDITIVE METHODS 22
     - 3.1.1 Alum Coagulation 22
       - 3.1.1.1 Alum Dosage 22
       - 3.1.1.2 Influent Fluoride Concentration 22
       - 3.1.1.3 Coagulant Aids 25
       - 3.1.1.4 pH 25
       - 3.1.1.5 Chemical Composition of Water 26
       - 3.1.1.6 Alum Feeding, Mixing and Flocculation 26
       - 3.1.1.7 Costs 27
       - 3.1.1.8 Case Studies 27
       - 3.1.1.9 Advantages 28
       - 3.1.1.10 Disadvantages 28
     - 3.1.2 Lime Softening 29
       - 3.1.2.1 Principle 29
       - 3.1.2.2 Operation 31
       - 3.1.2.3 Costs 32

3.1.2.4 Case Study 32
3.1.2.5 Advantages 32
3.1.2.6 Disadvantages 33
3.1.3 Other Chemicals 33
3.2 ION EXCHANGE/ADSORPTION METHODS 34
3.2.1 General 34
3.2.2 Bone 36
3.2.3 Synthetic Bone 37
3.2.3.1 Operating Conditions 38
3.2.3.2 Regeneration 39
3.2.3.3 Case Studies 40
3.2.3.4 Advantages 40
3.2.3.5 Disadvantages 41
3.2.4 Bone Char 41
3.2.4.1 Operating Conditions 41
3.2.4.2 Regeneration 42
3.2.4.3 Design Criteria for Small Installations 42
3.2.4.4 Costs 43
3.2.4.5 Case Study 43
3.2.4.6 Advantages 46
3.2.4.7 Disadvantages 47
3.2.5 Activated Alumina 47
3.2.5.1 Physiochemical Properties 47
3.2.5.2 Fluoride Removal Mechanism 48
3.2.5.3 Kinetics of Fluoride Removal 49
3.2.5.4 Fluoride Removal Isotherms 50
3.2.5.5 Removal Capacity 54
3.2.5.6 Influent Fluoride Concentration 57
3.2.5.7 pH 57
3.2.5.8 Competing Ions 59
3.2.5.9 Flow rate 62

3.2.5.10 Bed Size 63
3.2.5.11 Particle Size 64
3.2.5.12 Modes of Flow Application 64
3.2.5.13 Regeneration 64
3.2.5.14 Combined Treatment for Fluoride and Arsenic Removal 67
3.2.5.15 Recommended Operating Practices 69
3.2.5.16 Costs 72
3.2.5.17 Case Studies 75
3.2.5.18 Advantages 77
3.2.5.19 Disadvantages 77
3.2.6 Anion Exchange Resins 78
3.2.7 Other Media 81
3.3 DEMINERALIZATION METHODS 82
3.3.1 General 82
3.3.2 Reverse Osmosis 83
3.3.2.1 Principle and System Design 83
3.3.2.2 Performance and Operating Conditions 84
3.3.2.3 Costs 87
3.3.2.4 Case Studies 91
3.3.2.5 Advantages 92
3.3.2.6 Disadvantages 92
3.3.3 Electrodialysis 93
4. SUMMARY COMPARISON 96
REFERENCES 103

List of Tables

Table		Page
1	Fluoride levels of well water near Grande Prairie	12
2	Fluoride levels of well water in Hythe	13
3	Average concentrations of various groundwater constituents in the Grande Prairie area	17
4	Fluoride removal capacities of synthetic bone	38
5	Fluoride removal capacities of activated alumina	55
6	Plant data at Bartlett, Texas	76
7	Fluoride removal by reverse osmosis	86

List of Figures

Figure		Page
1	Topographic map of the Grande Prairie area	14
2	Bedrock geology and buried valleys in the Grande Prairie area	15
3	Groundwater fluoride levels in the Grande Prairie area 0 - 60 m depths, glacial drift	18
4	Groundwater fluoride levels in the Grande Prairie area 0 - 45 m depths, bedrock	19
5	Groundwater fluoride levels in the Grande Prairie area 45 - 90 m depths, bedrock	20
6	Groundwater fluoride levels in the Grande Prairie area 90 - 135 m depths, bedrock	21
7	Fluoride removal by alum coagulation Experimental results from Scott *et al.* (1937) and Nawalakhe *et al.* (1974)	23
8	Fluoride removal by alum coagulation Experimental results from Culp and Stoltenberg (1958) and Sollo *et al.* (1978)	24
9	Magnesium requirements for fluoride removal in lime-softening	31
10	Construction cost for bone char defluoridation plants	45
11	Chemical and media replacement costs for bone char defluoridation	46
12	Langmuir isotherm for fluoride adsorption on activated alumina Experimental results from Wu and Nitya (1979)	52
13	Langmuir isotherms for fluoride adsorption on activated alumina Experimental results from Singh and Clifford (1981)	53
14	Freundlich isotherm for fluoride removal on activated alumina Experimental results from Choi and Chen (1979)	54
15	Effects of pH and initial F^- concentration on fluoride capacity of activated alumina	59
16	Effects of SO_4^{2-} and Cl^- on activated alumina defluoridation	61

17 Concentration curves for caustic alkalinity and fluoride during caustic rinse and neutralization, Bartlett Plant, Texas 66

18 Concentration curves of a 2-stage activated alumina system during exhaustion phase 68

19 Concentration curves during typical pilot plant run, Gila Bend, Arizona 71

20 Construction cost for activated alumina defluoridation plants 73

21 Operation cost for activated alumina defluoridation 74

22 Fluoride capacity of a strong-base anion exchange resin 80

23 Construction cost for reverse osmosis plants 88

24 Energy requirments for reverse osmosis plants 89

25 Operation cost for reverse osmosis plants 90

26 Energy requirements for electrodialysis plants 94

27 Construction cost comparison for different processes
Cost data from Watson *et al.* (1974) 98

28 Land requirement comparison for different processes
Data from Watson *et al.* (1974) 99

29 Labour cost comparison for different processes
Cost data from Watson *et al.* (1974) 100

30 Total treatment cost comparison for different processes
Cost data from O'Brien (1983) 101

1. INTRODUCTION

Fluorine is the most electro-negative element and it does not naturally exist in the elemental state because of its high reactivity. The natural source of fluorine is minerals such as fluorspar, cryolite, fluorapatite, topaz and phosphorite (Jha and Jha 1982; National Health and Welfare 1978). Fluorides are widely distributed in water, soil and the atmosphere. On land, soluble fluorides naturally occur via leachates from rock; while in the air, fluorides are present in gaseous and particulate forms from volcanic emissions. Rainwater deposits atmospheric fluorides on soils and waters.

Environmental fluorides also orginate from industrial, municipal and agricultural activities. Industrial applications of fluorides are numerous, including various metal industries and the manufacture of electronics; bricks; tiles; ceramics; glass; wood preservatives; fertilizers; pesticides; and many others. These industries release fluorides to the environment via atmospheric emission, wastewater discharge, and disposal of industrial sludge. Fluorides can be leached into nearby waters from waste disposal sites or from mining operations. In many cases, fluoride is artificially added to municipal water supplies. Sewage, even after treatment, often contains higher fluoride content than the water supply (Rose and Marier 1977). The fluoride content in soils, originally arose from natural mineral constituents, is increased by the use of fertilizers. However, much of the fluoride in the soil is insoluble or tightly bound to soil particles (Jha and Jha 1982).

The fluoride content of natural waters varies locally in accordance to the source of water, the geological formation, the precipitation and the amount of evaporation. Unpolluted surface waters usually contain less than 0.3 mg/L naturally-occurring fluoride (Choi and Chen 1979; Jha and Jha 1982), and seldom exceed 1.0 mg/L (National Health and Welfare 1978). High natural concentrations are normally associated with groundwater in areas rich in fluorine-containing minerals (National Health and Welfare 1978). In Ohio, high fluoride groundwaters are generally found in limestone formation, and occasionally in gravel strata with underlying or overlying shales (Scott *et al.* 1937). The well data there show that the type of aquifer rather than the depth of well is the controlling factor. In Southern California, groundwaters in the arid and semi-arid areas are particularly high in fluoride content (Harmon and Kalichman 1965). For geothermal fluids, a wide range of fluoride concentrations have been reported (Choi and Chen 1979).

Fluoride is sometimes considered a "widespread, non-biodegradable and relatively persistent pollutant, which at low levels of contamination causes serious health problems difficult to cure" (Jha and Jha 1982). The fluorides in drinking water have significant public health impacts, especially regarding to children's teeth. Above the optimum concentration range for prevention of dental caries, the fluoride ion will cause mottling of children's teeth, a problem first related to drinking water by Dr. McKay (1926, cited throughout the literature). Ironically, the eventual recognition of fluoride as the actual cause of tooth mottling (1931) also later led to the discovery of its potential in preventing tooth decay. At a high enough concentration in drinking water, fluoride may cause bone problems in adults and children alike; the severity increases with higher concentrations. Many other health problems have also been related to fluorides in the water but without a strong base of evidence.

Excessive levels of fluoride have been found in well water supplies in the Grande Prairie area of Alberta. There is no evidence of industrial contamination. In the Village of Hythe, concentrations as high as 8 mg/L in private wells have been reported. In the immediate vicinity of the City of Grande Prairie, public wells serving the Hamlet of Clairmont and a number of mobile home parks (a total population of about 2,000) show fluoride concentrations in the range of 2.0 to 4.0 mg/L. These concentrations are sufficient to pose a serious threat to the development of young children's teeth. The likelihood of a large concentration of very young children living in the mobile homes is a particular concern. The record of well tests indicates that the fluoride content in well water has generally been increasing with increasing water consumption in the area.

Alberta Environment is committed to find a solution to this problem. This report is prepared for Alberta Environment as a review of the available treatment methods, which have been either proposed or used, for removing naturally-occurring fluorides from water supplies. The problems associated with fluorides in drinking water are also examined in detail.

2. NEEDS FOR FLUORIDE REMOVAL

2.1 HEALTH CONSIDERATIONS

2.1.1 Fluoride in Human Body

About 96 % of the soluble fluoride ingested and inhaled is absorbed through the gastro-intestinal and respiratory tracts (Newbrun and Zipkin 1976, cited by National Health and Welfare 1978). It enters the bloodstream by simple diffusion and the concentration in blood peaks within an hour after ingestion (Jha and Jha 1982). As much as 90 % of the ingested fluoride will be excreted within 24 hours, mostly in urine and some in perspiration and feces. Infants less than 3 years old have lower (50 %) fluoride excretion (Hodge *et al.* 1970, cited by National Health and Welfare 1978). Most of the fluoride retained is stored in hard tissues such as bones, teeth and nails. Fluoride is believed to be incorporated into bones and teeth by first combining with the calcium in blood and then depositing the insoluble calcium fluoride in the skeleton in combination with calcium phosphate to form fluorapatite and calcium fluorophosphate (Cook 1970). Some fluoride may also accumulate in soft tissues and organs such as kidneys and liver (Jha and Jha 1982).

Human blood normally contains about 0.15 mg/L fluoride of which only 10 % is free in the ionic form (Taves 1968, cited by Cook 1970). Rose and Marier (1977) reported that the plasma inorganic fluoride ion concentration responds rapidly and systematically to varying fluoride intake and to various physiological factors. High plasma F^- has been found in patients with renal insufficiency and those receiving fluoride administration or dialysis treatment with fluoridated water. The plasma F^- level also appears to increase with age. There have been reports of positive correlation between bone fluoride and plasma fluoride contents. Ingestion of fluoride is believed to alter the concentrations of several blood constituents as well.

Accumulation of fluoride in bones begins during gestation (Rose and Marier 1977). The level of fluoride intake by the mother during pregnancy may have a marked influence on the content of bone fluoride in the newborn (Hellstrom 1976, cited by Rose and Marier 1977). The accumulation of fluoride in the skeleton (including teeth) throughout the lifetime of a human is controlled by the level of fluoride intake, the receptivity of the bones, and the excretion efficiency of the kidneys. The bones are less receptive at old age (WHO 1970, cited by Rose and

Marier 1977) but the bone fluoride may still progressively increase with age because of declining kidney efficiency (Husdan *et al.* 1976, cited by Rose and Marier 1977). Fluoride accumulation is believed to affect the structure and chemical composition of bones and teeth.

Urinary excretion of fluoride depends on the total fluoride intake, the form of fluoride ingested, previous exposure, and the general health. Normally, the fluoride concentration in the intake water approximates the fluoride concentration in the urine (Hodge *et al.* 1970, cited by National Health and Welfare 1978). People exposed to excessive amounts of fluoride continue to exhibit abnormally high concentrations of fluoride in their urine even after normal intake resumes (National Health and Welfare 1978). However, some of the additional fluoride is permanently deposited in the skeleton and is not readily excreted even after reduction in fluoride intake (National Academy of Sciences 1971, cited by National Health and Welfare 1978). Fluoride clearance through urine increases with age, possibly due to slow saturation of the bones with fluoride, until about age 50 (Hanhijarvi 1975, cited by Rose and Marier 1977). Diminishing renal function at older ages is responsible for a slight decline thereafter. Rose and Marier (1977) summarized reports that fluoride ingestion resulted in changes in distribution of other components found in urine.

The tendency of fluoride to accumulate in organisms may have serious chronic toxic effects resulting from small doses being ingested over a long time. The known biological effects of fluoride are reviewed in the following sections.

2.1.2 Dental Effects

Small amounts of fluoride ion in drinking water (about 1 mg/L in Canadian climates) can substantially reduce dental caries in children and in adults who consumed fluoridated water during childhood (Prival 1974). Once incorporated into the crystal structure of the dental enamel, fluoride increases the resistance of the enamel to acids excreted by bacteria in dental plaque. It may actually inhibit the enzymes of the bacteria, thereby preventing the conversion of sugar into acids (Jenkins 1970, cited by Prival 1974).

Excessive fluorides in drinking water, on the other hand, will give rise to dental fluorosis in children's teeth, a term associated with mottled enamel and disfigurement of the permanent teeth. The severity depends on the fluoride concentration at normal water consumption. At the concentration for maximum reduction of caries, only a small percentage

of the children may be affected by a mild form of dental fluorosis. In the mildest forms of dental fluorosis, the opaque, white areas formed on the normally translucant surface (Prival 1974) are hardly conspicious. As the fluoride level goes up, more children will be affected and more visible mottling with progressively darker discolouration will occur. The appearance may become objectionable at 1.5 mg/L (National Health and Welfare 1978). At about 2 mg/L, brown stains emerge (Dean 1942, cited by Prival 1974). In the severe cases associated with high fluoride levels, the teeth show absolutely black discolouration, deep confluent pitting and attrittion of the enamel (Prival 1974; Scott *et al.* 1937).

Fluoride accumulation on dental and skeletal tissues is most rapid during formation and mineralization. Mottling and disfigurement of teeth can only occur during the period of enamel formation, up to about 12 years of age (Prival 1974), but the defects become permanent for life.

2.1.3 Skeletal Fluorosis

Teeth are not the only part of the skeleton system where fluoride is deposited. While dental fluorosis is the most common manifestation of chronic fluoride intoxication, bones are also affected by excessive fluoride intake. However, the intoxication is not limited to a particular period as the cellular activity of bones continues throughout the lifetime.

Fluoride incorporation in bones is associated with thickening of the bones due to an increase in the average size of the inorganic apatite crystals (Eanes *et al.* 1965, cited by Prival 1974) as additional calcium, in the form of calcium fluoride, is being deposited to form fluorapatite (Cook 1970). The bone density is also increased (Prival 1974; Singh and Clifford 1981). At relatively low fluoride levels in drinking water, these phenomena can be regarded as an added protection of the bone material against dissolution in the surrounding fluids (Prival 1974). Yet, fluoride is not a cure for osteoporosis (Nordin 1969, cited by Cook 1970) - a bone weakening problem - especially when calcium intake remains deficient (Rose and Marier 1977). Areas of both over- and under-calcification may develop due to interference of fluoride with resorption and exchange of calcium, a situation which does not improve osteoporosis (Cook 1970).

Fluoride-induced bone growth is abnormal. It is weaker and more brittle (Rose and Marier 1977) than the better structured bone material it has replaced (Prival 1974). It is said

that an intake of 10 mg fluoride per day for many years will develop this growth into skeletal fluorosis (Cook 1970). The severity of skeletal fluorosis has been described in numerous reports (Cook 1970; Prival 1974; Rose and Marier 1977). It includes the early symptoms of rheumatic or arthritic pains; painful and disabled joints; and progressively stiff back as a result of hypertrophic changes starting from the pelvis to the entire spine. In more severe cases, extra growth on the ribs restricts breathing; and thickened vertebrae compress the spinal nerves and lead to neurological damage. Severe skeletal fluorosis is uncommon to North America. However numerous forms, including cases of crippling fluorosis, have been observed in various parts of India (Prival 1974; Rose and Marier 1977), associated with fluoride levels in water ranging from less than 2 mg/L to more than 10 mg/L. Excessive fluoride intake from all sources and nutritional deficiencies may be responsible for aggravating skeletal fluorosis in India.

Inadequate dietary intake of calcium, magnesium and vitamin C may promote or worsen skeletal fluorosis (Cook 1970; Rose and Marier 1977). According to Cook, the exchange and resorption of calcium between blood and bones, which are necessary mechanisms to maintain a constant level of calcium in the blood and in all tissues for correct functioning, are inhibited by fluoride incorporation in bones. In case of low calcium supplementation to the system, chronic fluoride intoxication results. A similar effect possibly applies to magnesium and vitamin C. Fluoride intake is reported to increase the metabolic requirements for calcium, magnesium and vitamin C (Rose and Marier 1977). Calcium and magnesium in drinking water may make up a good portion of the total dietary intake of these elements. The hardness of water has been reported to offer a protective effect against the development of fluorosis (Jolly *et al.* 1968, cited by Rose and Marier 1977).

2.1.4 Kidney-related Problems

Marier (1977), and Rose and Marier (1977), reported on the particular susceptibility of people with impaired kidney function to fluoride intoxication. People suffering from bilateral kidney disease accumulate higher then normal amounts of fluoride in the bones as excretion is impeded. The use of fluoride-bearing water for artificial-kidney hemodialysis on a long-term basis results in high bone fluoride uptake. The complications include bone ostemalacia and spontaneous bone fractures. Cases of skeletal fluorosis have been observed in people suffering from nephropathic Diabetes Insipidus, including some young children. Polydipsia (excessive

thirst) and polyuria (excessive fluid loss) are two commonly associated syndromes. These syndromes, sometimes coupled with inadequate kidney function, result in high fluoride intake through excessive water consumption and in abnormally high fluoride retention.

Fluoride may actually be a causative agent of kidney malfunction. Rose and Marier (1977) reviewed studies indicating that there is a recognized possibility that fluoride can complicate or actually induce nephropathy, and that it may aggravate kidney disease. There has been evidence of fluoride-induced polydipsia and that fluoride may cause nephogenic Diabetes Insipidus.

As fluoride is concentrated by the kidneys for urinary excretion, it is conceivable that the kidney itself is vulnerable to chronic fluoride intoxication (Hodge and Smith 1965, cited by Prival 1974). Stones containing very high amounts of fluoride, which has apparently aided their growth, have been found in kidneys (Taylor 1954, cited by Cook 1970) and in urinary tracts (Smith *et al.* 1960, cited by Prival 1974). Again, people who already have abnormal kidney function are susceptible to further kidney damage by chronic fluoride ingestion. At fluoride levels normally encountered in water, the general population is not likely to suffer any effects on kidneys (Prival 1974).

2.1.5 Effects on Enzymes

Cook (1970) reported on work showing that fluoride is an inhibitor of many essential enzyme systems in the body even at low concentrations. The inhibitory action is probably the removal of the metal required for the enzyme function. Body functions affected are the normal working of the muscles and cell membranes, carbohydrate metabolism, bone formation, protein metabolism, blood formation and reproduction. Vitamin B and some amino acids, which are essential for certain processes in the body, may also be destroyed. Chronic fluoride ingestion can also interfere with the normal enzyme-dependent functioning of the thyroid, parathyroid, parotid and adrenal glands. Studies relating fluorosis to symptoms of thyroid hypofunction have been reported by Rose and Marier (1977). Structural changes in anterior brain cells and muscle cells have been discussed by Franke *et al.* (1973, cited by Rose and Marier 1977).

While recognizing fluoride as a potent inhibitor of many enzymes in the test tube, Prival (1974) dismissed its effectiveness within the living organism. Most of the fluoride in body fluids is bound and rendered non-reactive. At least, the inhibition of serum enzymes

appears to be unlikely at reasonable fluoride intake levels, as a constant fluoride concentration is maintained in the blood if the fluoride concentration in the water ingested does not exceed 2 mg/L (Singer and Armstrong 1960, cited by Prival 1974). Ferguson (1971, cited by Prival 1974) observed a transient effect on serum alkaline phosphatase in response to a small increase in fluoride intake. Ferguson suggested that fluoride may temporarily lower the enzyme levels but not inhibit the enzyme itself.

2.1.6 Other Implications

Long-term epidemiological surveys have not revealed any statistically significant correlation between fluoride in water and mortality or morbidity (Prival 1974). Fluorides might be considered possible carcinogens based on observations of their effects on animal and plant cells but epidemiological studies attempting to correlate cancer deaths with fluoride exposure via drinking water have led to conflicting but no conclusive findings (National Health and Welfare 1978; Rose and Marier 1977). Fluoride has the tendency to accumulate in soft tissues that have been calcified, but there is no evidence that it actually promotes hardening of the arteries, a phenomenom often related to heart disease (Prival 1974).

Genetic effects have been observed in animals, but only at much higher fluoride levels than are found in human body fluids (Jagiello *et al.* 1974, cited by National Health and Welfare 1978). The mutagenicity of fluoride in some organisms is believed to be related to inhibition of DNA synthesis (Oyen and Laland 1969, cited by National Health and Welfare 1978). Mongolism in humans is a result of genetic changes. Dr. Rapaport (1956, cited by Prival 1974) linked monogoloid births to areas of high-fluoride waters. However, the data are not considered adequate to demonstrate that fluoride is the real cause of this syndrome (Prival 1974).

Cases of allergic reactions, including hives; intestinal pain; nausea; headaches; mouth ulcers; nasal disturbances; irritation; fatigue; excessive thirst; muscular pain and skin sensitivity, have been linked to fluorides in the water (Cook 1970). These are the symptoms of disturbances to the central nervous system, mucous membrane, or the neuromuscular system. Prival (1974) reported these claims as controversies which have been neither proven nor disproven.

2.2 WATER USERS AFFECTED BY FLUORIDES IN THE WATER

The foregoing discussion suggests that chronic ingestion of fluoride affects people differently in accordance to age and health conditions. As far as dental effects are concerned, children in the tooth formation years are most susceptible. Fluoride supplementation or removal in school water supplies alone, or specially bottled water for children, have been suggested in many incidences. Patients receiving hemodialysis treatment cannot tolerate long-term fluoride input from the dialysis water; fluoride-free water is recommended for the dialysis treatment. People with Diabetes Insipidus are particularly susceptible to even very low levels of fluoride in the drinking water. In general, people with kidney abnormalities may have to resort to a drinking water that contains a much lower fluoride concentration than that prescribed as optimum for a normal person.

There is a tendency of escalating the fluoride content in the human food-and-beverage chain by using fluoride-bearing waters in the food and beverage processing industry (Bratton 1953; Marier 1977). Bratton voiced his concerns over the effects of fluoridated water on certain industrial uses, such as wet-milling of corn; yeast production; and manufacturing of pharmaceutical and medicinal products. There may be difficulties in the processing itself or problems of complying with the food and drug regulations. Weir (1953) stated that at the fluoride concentrations recommended for public water supply, industrial users would not be significantly affected, nor would the fluoride in processed foods and beverages make a significant addition to the normal diet.

High natural fluoride concentrations are mostly found in groundwater. Consequently, high fluoride problems are most frequently located in small communities, trailer parks, isolated households, etc., which rely on wells for water supply. Ironically, these are the populations that do not have the economic base or trained expertise to support a fluoride removal treatment system.

2.3 OPTIMUM AND PERMISSIBLE LEVELS OF FLUORIDE

The objective and maximum acceptable concentrations of fluoride in drinking water are set on the basis of dental effects and supported by epidemiological studies. The maximum level is the level at which dental fluorosis in children is believed to become significant. At this level, abnormalities in bones and other possible chronic intoxication effects on the body are unlikely

for the general population. The optimum level is the level at which enough fluoride is present to greatly reduce dental caries while still being safe relative to fluorosis.

The extent of fluoride intake via drinking water depends on the amount of water consumed which in turn relates to air temperature. Higher temperatures increase fluid loss in the body through vaporization and therefore increase water intake demand. For most Canadian communities, where the annual mean daily maximum temperature is greater than 10 °C, the 'Guidelines for Canadian Drinking Water Quality' (National Health and Welfare 1978) recommend an objective concentration of 1.0 mg/L for the fluoride ion. In cooler climates, the objective concentration is 1.2 mg/L in order to achieve a comparable beneficial effect. The maximum permissible level is set at 1.5 mg/L in all cases. In North America, possible bone changes in a healthy person are generally believed to occur when the fluoride level in drinking water exceeds 8 mg/L.

These prescribed concentrations are arbitrary to some extent when one considers the many factors other than drinking water that can also influence fluoride intake. Exposure to airborne fluorides is usually minimal except in certain specific industrial areas. However, the fluoride in foods remain a sizable portion of the dietary intake depending on individual food habits. This is particularly true when increased food and beverage products processed from fluoridated water are available on the market. All natural foods contain at least traces of fluoride. Fluorides in the atmosphere, irrigation water and fertilizers may add to the fluoride content in food crops. The method of cooking can also concentrate fluoride. Toothpastes, tooth powders, mouthwashes, and vitamin supplements are among the fluoridated products that can influence fluoride intake in a person. In Canadian communities served by artificially fluoridated water, the average total daily intake of fluoride is 2.7 mg for adults and 2 mg for children (Burgess, cited by National Health and Welfare 1978). The U.S. Federal Food and Drug Administration (cited by Calabrese 1983) states that 2 to 3 mg of dietary fluoride per day should be a safe amount for young children.

Calabrese (1983) commented on the U.S. Environmental Protection Agency (EPA) drinking water standard for fluoride, which is set on a similar basis as the Canadian standard. He argued that the existing standard did not allow an adequate safety factor to account for the apparent escalation in dietary intake of fluoride from all sources. He indicated that healthy individuals may be ingesting as high as 5 mg per day total fluoride as a result of the use of

fluoridated water in food processing.

2.4 FLUORIDE LEVELS IN ALBERTA

Compiled data from various provinces and territories of Canada indicate that the average natural fluoride concentration in water supplies is highest in Alberta (National Health and Welfare 1978). The highest fluoride concentrations in Canada are also found in Alberta waters. Alberta Environment (Prent 1977, cited by National Health and Welfare 1978) reported in a 1976 water survey summary that fluoride concentrations in tap water of Alberta ranged from 0.1 to 3.3 mg/L. Statistics supplied by the High Fluoride Commitee (1983) showed that 28 Alberta municipalities with a total population (1976) of 19,000 had natural fluoride concentrations exceeding 1.5 mg/L and up to more than 4.0 mg/L in their water supplies. Most of these were well water supplies. The recommended fluoride level for drinking water in Alberta is 1.0 mg/L (Alberta Fluoridation Regulations).

The Grande Prairie area is one of the high-fluoride problem areas in Alberta. Information has been gathered from Alberta Environment (1983) and from a report by GCG Engineering Partnership (1980). About 2,000 people in the areas surrounding Grande Prairie consume water from public wells that report fluoride concentrations in the 2.0 to 4.0 mg/L range. Table 1 shows the changing fluoride levels at these wells. There are also indications of high-fluoride well water in nearby areas. Table 2 shows the fluoride levels sampled from individual wells in the Village of Hythe, about 40 km to the northwest. Both tables indicate that there is a general trend of increase in the fluoride levels. This trend is attributed to increasing water consumption. The Grande Prairie Health Unit considers that a fluoride concentration between 1.5 and 2.4 mg/L is not serious but does not recommend the use of fluoridated products in the diet of children below age 12. For concentrations exceeding 2.4 mg/L, the Health Unit advises the use of an alternate water supply for drinking and cooking.

There has not been any hydrogeological study to investigate this high-fluoride problem in the Grande Prairie area although general groundwater conditions are surveyed in two reports (Hackbarth 1976, 1977). The topography and geology of the survey area are shown in Figures 1 and 2, respectively. Over much of the area, the bedrock source of water supplies is limited to the Wapiti Formation which consists of feldspathic sandstone, bentonitic mudstone, scattered coal and nonmarine. Much of the groundwater movement is believed to occur in the fractures

Table 1. Fluoride levels of well water near Grande Prairie

(Alberta Environment 1983)

COMMUNITY	DATE	WATER SOURCE	DEPTH OF WELL	FLUORIDE (mg/L)
T & E Trailer Park	Sept 18/74	Well		1.97
	Aug 13/75	Well	400'	2.10
	Feb 5/80	Well		2.25
	Feb 20/80	Well	425'T.D. 250'W.L.	1.89
	*Aug 18/81	Well #1		2.6
	*Aug 18/81	Both Wells		2.6
Eldoe's Trailer Park	July 13/70			.56
	July 23/70	Well	150'T.D. 130'W.L.	.48
	Oct 24/72	Well	210'T.D. 118'W.L.	---
	Sept 18/74	Well	220'T.D. 118'W.L.	.95
	April 27/81	Well		2.70
	*Aug 18/81	Well in White Shed		3.6
Swan City Trailer Park	Sept 2/80			2.95
	Oct 29/80			3.26
	*Aug 18/81	Well #1		3.6
	*Aug 18/81	Well #2		4.0
	*Aug 18/81	Well #3		4.0
Triple L Mobile Home Park	April 25/79 (4 p.m)	Well	255'T.D. 183.85'W.L.	2.43
	April 25/79		255'T.D. 185'W.L.	2.33
	April 25/79 (12 a.m.)		200'T.D. 170'W.L.	2.13
	Aug 18/80		264'T.D.	2.45
	Dec 8/80		360'	3.93
	April 21/81			3.65
	June 23/81		360'	3.97
	July 21/81		360'T.D. 50m W.L.	3.75
Clairmont (Hamlet in County of Grande Prairie)	Jan 24/79			0.92
	Jan 22/80			2.00
	Jan 22/80			2.00
	Feb 23/81			3.06
	Feb 23/81			2.94
	*Aug 17/81			2.6

T.D. indicates Total Depth W.L. indicates Water level

* indicates samples analysis by Dental Department. Samples were submitted to Environment Centre Laboratory on same day.

Mobile Home Parks are from adjacent to city's east side to 5 miles east of Grande Prairie.

Clairmont is 4 miles north of Grande Prairie

Table 2. Fluoride levels of well water in Hythe

(Alberta Environment 1983)

POINT OF SAMPLING	DATE	DEPTH OF WELL	FLUORIDE (mg/L)
Village Office	March/69	T.D. 100' W.L. 10'	1.14
	Aug 29/81		1.8
Hospital	No date	T.D. 220'	1.3
	Aug 29/81		3.6
Old Folk's Home	Oct/75		1.49
	Oct/77		1.92
	Aug 29/81		2.2
Day Care	April/76		1.5
	Aug 29/81		2.2
Pioneer Home	Jan/80		1.33
	July/80		1.65
	Aug 29/81		2.4
George Dane	Aug 29/81		4.2
Andy Tschetter	Aug 29/81		4.0
Seven Lakes Motel & Cafe	Aug 29/81		8.0

T.D. indicates Total Depth W.L. indicates Water Level

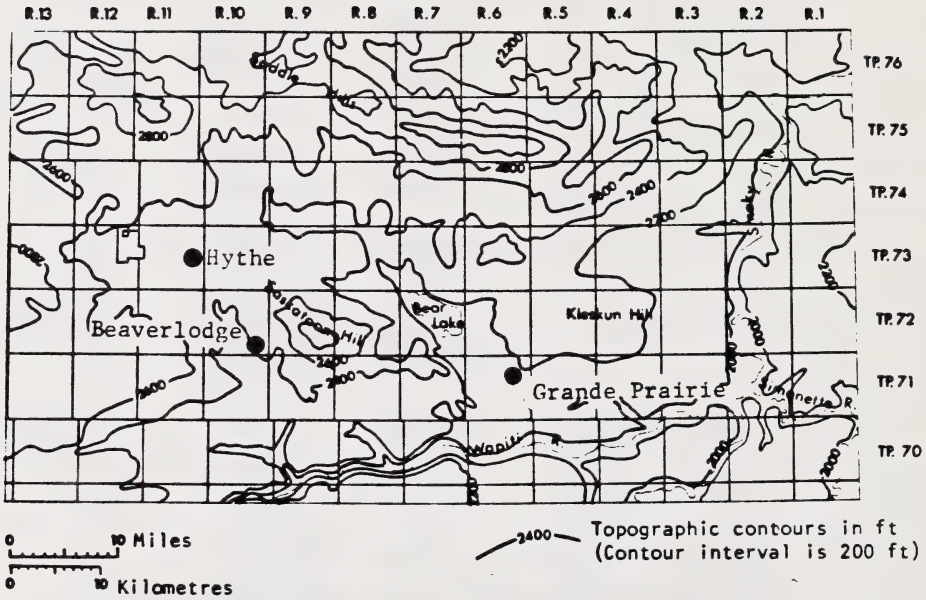


Figure 1. Topographic map of the Grande Prairie area

(Hackbarth 1977)

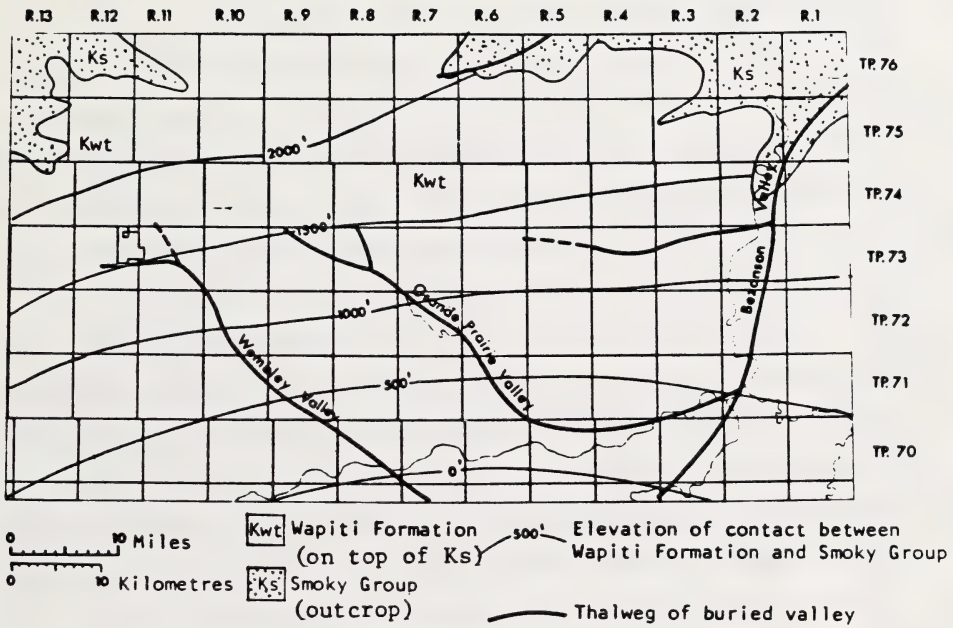


Figure 2. Bedrock geology and buried valleys in the Grande Prairie area

(Hackbarth 1977)

connecting the sand lenses in the Wapiti Formation. The average concentrations of various groundwater constituents are listed in Table 3. There are however localized areas of higher concentrations. The areal distributions of fluoride contents at various depths are mapped in Figures 3 to 6. These charts indicate that fluoride concentrations are higher in aquifers that occur at greater depths in the bedrock. The concentrations in many areas are expected to exceed the recommended maximum of 1.5 mg/L from depths greater than 90 m. Between 90 and 135 m depths, Figure 6 shows a band of values up to 3.0 mg/L extending southward from Hythe and from Beaverlodge to Grande Prairie. In Figure 3, a localized area of high fluorides occurs at shallow depths in the glacial drift southeast of Beaverlodge. This is believed to be associated with an upward groundwater flow from a depth of at least 135 m.

The low-fluoride areas generally follow the buried valleys that cross the survey area. The thalwegs of these buried valleys are shown in Figure 2. These valleys contain considerable deposits of gravel or sand. The groundwater flow patterns, especially near the surface, suggest that the Wembley and Grande Prairie Valleys may act as regional groundwater drains. Excellent groundwater yields may be available from the deposits of the buried valleys where the fluoride levels are also generally the lowest.

The groundwater chemistry of the study area is predominantly sodium bicarbonate with a tendency of being calcium bicarbonate in areas of thick glacial drift. Except in the northeastern portion of the study area generally north of Saddle Hills, the groundwater exhibits fairly good quality on the average. However, total dissolved solids, sulphate, alkalinity and sodium concentrations are slightly higher than the standards in most areas, especially at shallow depths. Except for fluoride, the water quality appears to improve with depth, most noticeably in terms of total dissolved solids. However, any attempt to locate a water source of high overall quality at great depths may be disappointed by the occurrence of excessive fluorides.

There are two solutions for a high-fluoride problem in groundwater. One solution is to use an alternate water source, at least for drinking and cooking purposes. Locating a suitable groundwater source would require an updated and detailed hydrogeological study of the area. The feasibility of a surface source or hauling water from a low-fluoride source may also be considered. The other solution is to treat the high-fluoride water. Available technologies for removal of fluorides are reviewed in the remainder of this report.

Table 3. Average concentrations of various groundwater constituents in the Grande Prairie area

(Hackbarth 1976)

Parameter	Glacial drift	Bedrock 0-150'	Bedrock 150-300'	Bedrock 300-450'	Alberta Standards*	Number of Samples: Drift	Bedrock 0-150'	Bedrock 150-300'	Bedrock 300-450'
Total dissolved solids	1227	1251	1130	936	1000	210	288	287	79
Hardness (as $CaCO_3$)	274	164	93	49	500	210	288	287	79
Sulfate	384	394	234	87	250	210	288	287	79
Chloride	12	10	15	16	250	210	288	287	79
Alkalinity (as $CaCO_3$)	627	691	772	723	500	210	288	287	79
Fluoride	0.5	0.7	1.0	1.6	1.5	153	218	223	59
Calcium	60	33	21	18	200	146	216	224	69
Magnesium	22	14	6	4	150	146	216	224	60
Sodium	377	399	394	359	300	133	192	195	52
Potassium	2.9	2.2	1.7	1.6	-	133	192	195	52
Carbonate (as $CO_3^{=}$)	1.9	7	6.8	7.6	**	133	192	195	52
Bicarbonate (as HCO_3^{-})	836	829	913	870	**	133	192	195	52

(all concentrations in mg/L)

Explanation: *Standards from: Canada Department of National Health and Welfare (1969).
**Carbonate Plus Bicarbonate (as $CaCO_3$) are subject to the same standard as alkalinity.
Data includes analyses from wells in Townships 69 through 76 only.
Glacial drift - samples obtained from a well terminating in glacial drift.
Bedrock - Water samples obtained from wells 0 to 150, 150 to 300, or 300 to 450 feet deep which terminate in bedrock. (ie. about 0 - 45, 45 - 90, 90 - 135 m depths)

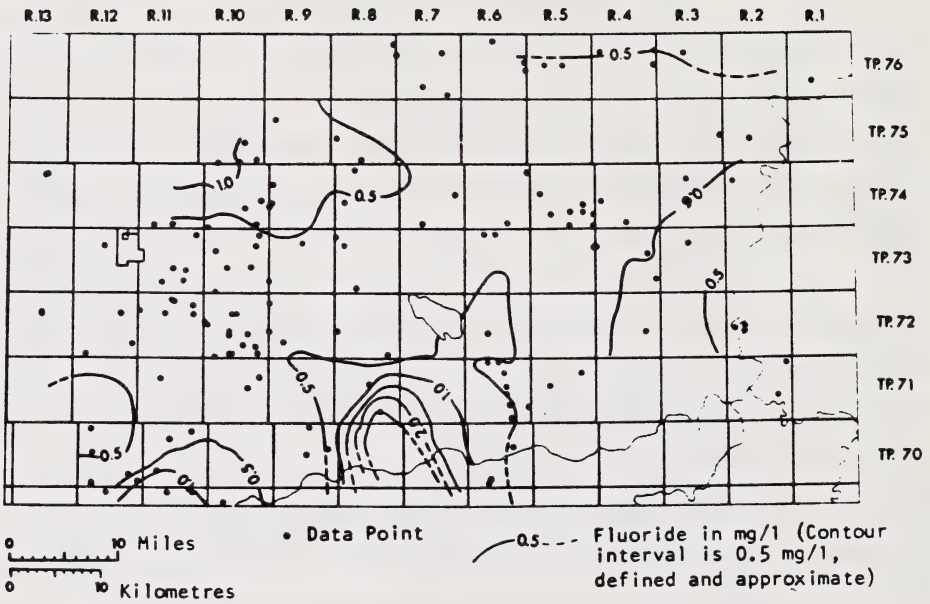


Figure 3. Groundwater fluoride levels in the Grande Prairie area

0 - 60 m depths, glacial drift

(Hackbarth 1977)

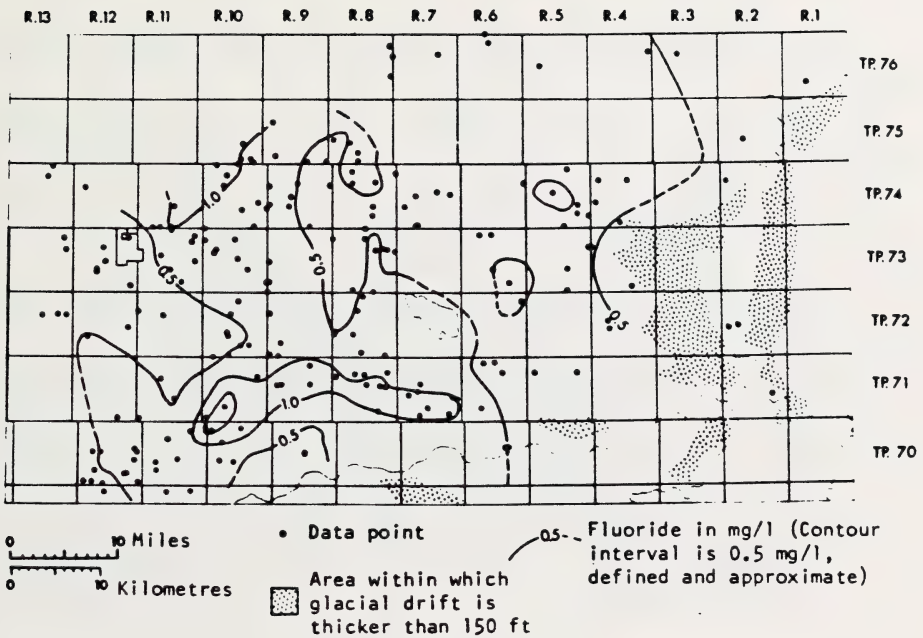


Figure 4. Groundwater fluoride levels in the Grande Prairie area

0 - 45 m depths, bedrock

(Hackbarth 1977)

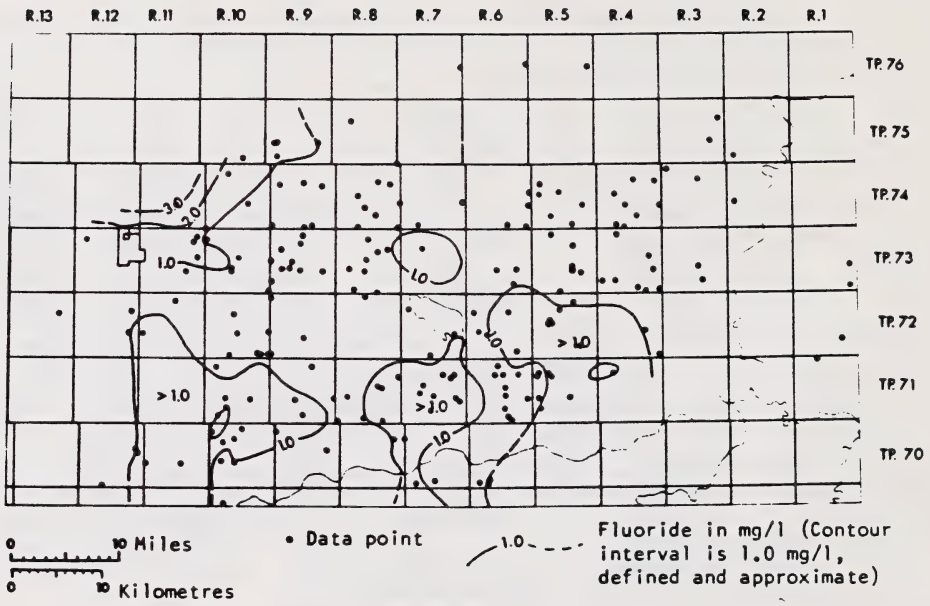


Figure 5. Groundwater fluoride levels in the Grande Prairie area

45 - 90 m depths, bedrock

(Hackbarth 1977)

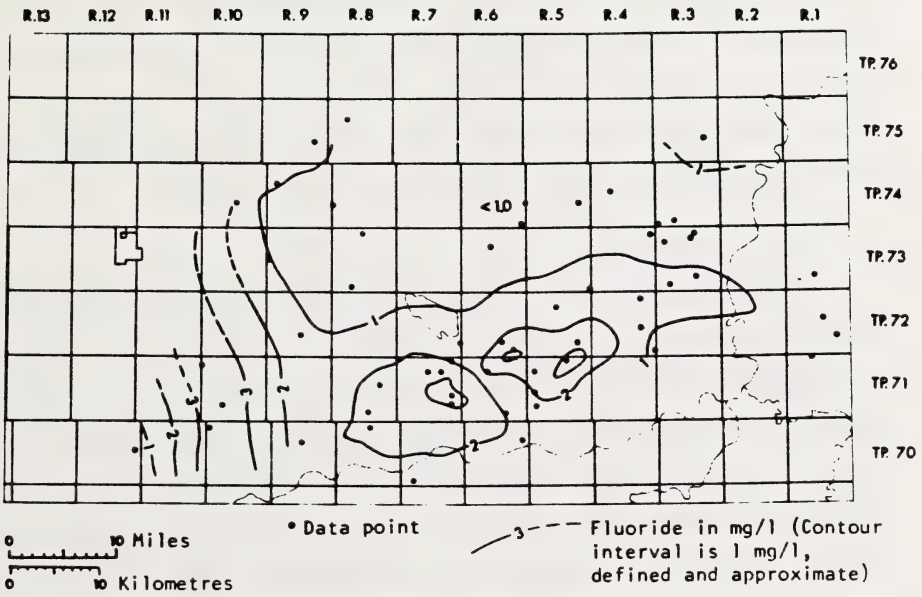


Figure 6. Groundwater fluoride levels in the Grande Prairie area

90 - 135 m depths, bedrock

(Hackbarth 1977)

3. FLUORIDE REMOVAL TECHNOLOGIES

3.1 ADDITIVE METHODS

3.1.1 Alum Coagulation

Aluminum sulphate, commonly known as alum, is normally used in water treatment for the removal of turbidity and colour. The addition of alum during the coagulation process yields a flocculant precipitate of hydroxy-complexes of aluminum. This can co-precipitate or adsorb other constituents on the floc. For fluoride removal, the mechanism is believed to be the formation of an aluminum fluoride complex or adsorption on the alum floc. The fluoride may be removed with the floc in the sedimentation or filtration step. Once floc has precipitated it will have no further fluoride removal capacity. The use of recirculated sludge therefore will not achieve significant fluoride reduction (Culp and Stoltenberg 1958).

3.1.1.1 Alum Dosage

Early investigations on the ability of aluminum compounds to remove fluorides from drinking waters were conducted by Boruff (1934). With alum coagulation, the alum dosages were found a little in excess of the amounts normally required for the removal of colour and turbidity. Later studies by other workers have shown much higher alum dosage requirements. The alum dosage is actually a function of many controlling conditions. These include the initial fluoride concentration, effluent fluoride level desired, pH, alkalinity, chemical composition of the water and methods of chemical feeding and mixing. As a result of different test conditions, widely varied dosages have been reported. The alum dosages and associated fluoride removal efficiencies reported by some researchers are plotted in Figures 7 and 8. There is a general agreement that large doses of alum are required to remove small amounts of fluorides, much greater than those commonly used for turbidity and colour removal. These plots also indicate that the incremental efficiency of fluoride removal decreases with higher dosages.

3.1.1.2 Influent Fluoride Concentration

According to Hung (1981), an effective coagulant for fluoride removal should give a positive slope when the ratio of influent fluoride concentration to coagulant dosage is plotted against the equilibrium fluoride concentration. Among a number of coagulants Hung

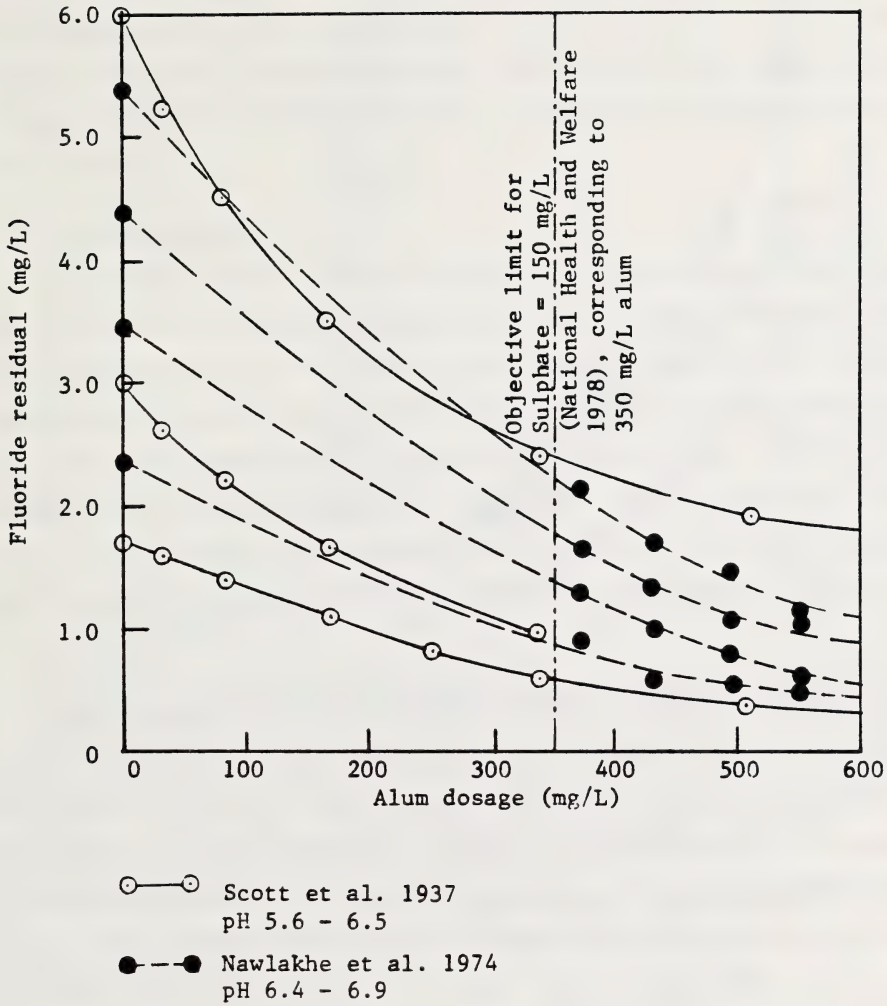


Figure 7. Fluoride removal by alum coagulation

Experimental results from Scott *et al.* (1937) and Nawalakhe *et al.* (1974)

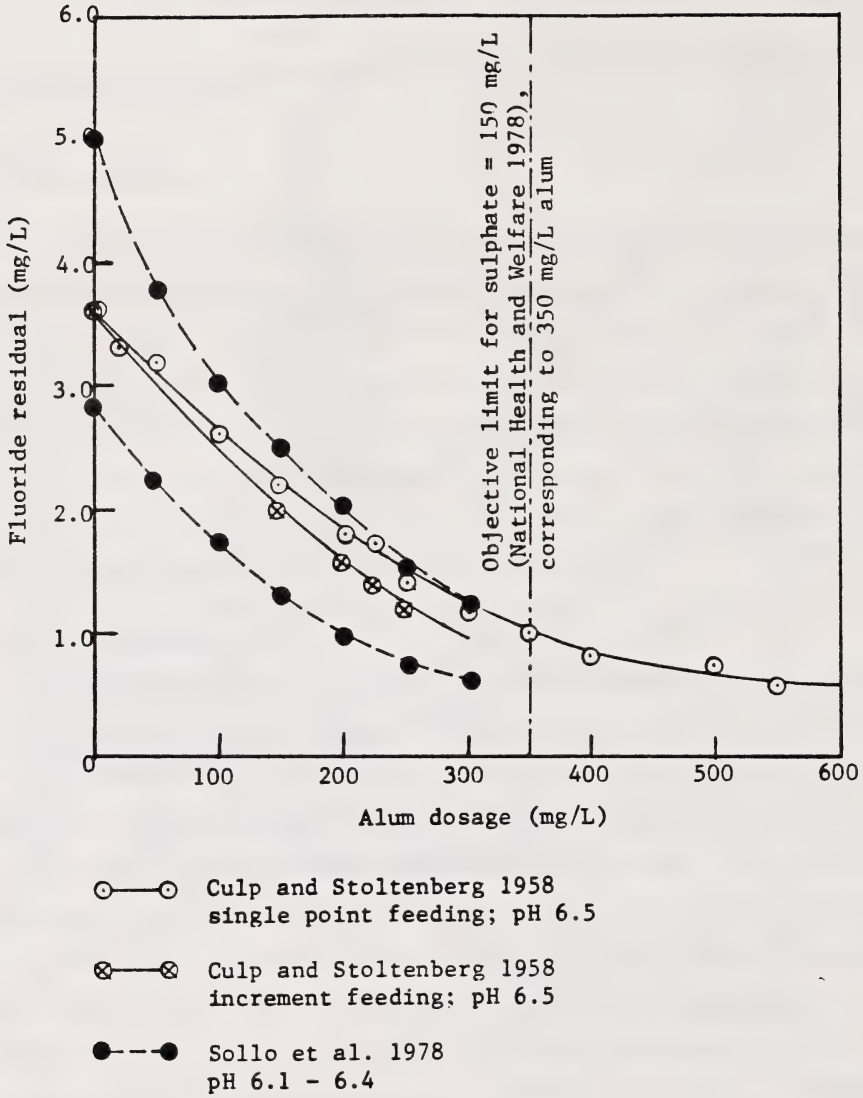


Figure 8. Fluoride removal by alum coagulation

Experimental results from Culp and Stoltenberg (1958)

and Sollo *et al.* (1978)

investigated, alum was found to show such characteristics. Naturally, for a fixed equilibrium fluoride concentration, the alum dosage required will increase with higher initial fluoride concentrations. Sollo *et al.* (1978) has shown that the efficiency of fluoride removal is dependent on the initial fluoride concentration. Fluoride removal by alum is more effective at lower initial fluoride concentrations but becomes impractical for an initial concentration greater than 4 or 5 mg/L.

3.1.1.3 Coagulant Aids

Maier(1947) reported some success in the use of clay and activated silica as coagulant aids. Culp and Stoltenberg (1958) performed coagulation tests using activated silica, bentonite, hydroxyethyl cellulose and Fuller's earth in various dosages as coagulant aids. They found no particular advantage in using the aids if satisfactory coagulation and settling could be achieved by the alum alone. Sollo *et al.* (1978) reported that when an anionic, cationic or non-ionic polyelectrotyte was added immediately after the alum, as a coagulant aid, only 1 to 2 % better removal could be achieved because of improved flocculation and sedimentation. Anionic and non-ionic polyelectroytes were more effective while all types shortened the sedimentation time.

3.1.1.4 pH

The ability of alum to remove fluorides is affected by the pH at flocculation. The optimum pH has been reported in the range of 6.0 to 7.5 (Boruff 1934; Culp and Stoltenberg 1958; Sollo *et al.* 1978). If the required alum dosage produces a pH in the optimum range, no pH pre-adjustment will be necessary. In any event, the treated water will have to be neutralized by lime to avoid corrosion troubles. Culp and Stoltenberg (1958) suggested a lime dosage of 15 mg/L, and that it should be added near the end of the flocculation period to prevent calcium interference with fluoride removal.

The role of pH in fluoride removal has been explained by several researchers. Boruff (1934) recognized the fact that in the slightly acid range the alum floc mainly consists of basic aluminum hydroxides and carries large quantities of other negative ions in its structure. pH is also believed to influence the settleability of the floc (Kempf *et al.* 1936). Fluoride removal depends, in part, on the efficiency of alum flocculation. Culp and Stoltenberg (1958) found that the pH corresponding to the most efficient flocculation time coincided with the optimum pH for fluoride removal. Residual aluminum was also minimized in the optimum pH range,

thereby reducing the possibility of depositing in the watermain.

3.1.1.5 Chemical Composition of Water

Defluoridating natural waters of different chemical makeups by alum may result in varied fluoride removal efficiencies or require different alum dosages for a comparable fluoride reduction. Presumably, some species may interfere with fluoride removal. Maier (1947) reported that highly mineralized groundwaters with excessive fluorides would limit the effectiveness of alum in removing fluorides. Boruff (1934) found that chloride and sulphate concentrations as high as 1,000 mg/L had no effects on the removal of fluorides. Another study (Boruff *et al.* 1937) indicated that while fluoride was readily removed by alum coagulation as sodium fluoride, certain cations associated with the fluoride ion, such as calcium and magnesium, greatly hindered the completeness of fluoride removal. The removal of calcium and magnesium ions by zeolite softening prior to alum coagulation was not sufficiently complete to convert small amounts of fluoride to sodium fluoride and therefore did not improve subsequent fluoride removal. Other reports also generally agreed that hardness in water would interfere with fluoride removal by alum. In constrast, Sollo *et al.* (1978) showed that the presence of calcium actually improved fluoride removal slightly. Culp and Stoltenberg (1958) indicated that iron and manganese would not interfere with fluoride removal by alum; these metals may also be removed in the process by chlorine addition.

Nawlakhe *et al.* (1974) observed that alkalinity was generally high for fluoride-bearing raw waters in India. For the same degree of fluoride reduction, the alum requirement increased with an increase in alkalinity. Nawlakhe *et al.* (1975), and Nawhakhe and Bulusu (1978), examined a number of other possible interferences. The effects of sulphate, chloride, total available chlorine, calcium, polyphosphates, nitrate, silicate, organic matter and temperatures were reported. Only increased silicate or higher temperatures resulted in lower fluoride removals. No effects were observed for the other parameters.

3.1.1.6 Alum Feeding, Mixing and Flocculation

Good mixing and flocculation are necessary to maximize fluoride removal. Slow addition and adequate stirring of the alum are essential for promoting immediate contact between the aluminum hydroxides and the fluoride ions for better flocculation. Culp and Stoltenberg (1958) have shown that the mixing time itself is not as important providing the

above requirements are matched. In addition, incremental feeding during slow mixing instead of application at a single point during rapid mixing may save the alum dose by 10 % for the same fluoride reduction (Figure 8). This is probably the result of better contact between aluminum and fluoride ions during the initial formation of the floc particles, and also of more complete coagulation.

3.1.1.7 Costs

Fluoride removal by alum coagulation is accomplished in conventional coagulation and sedimentation facilities. These include chemical storage facilities; feeders; mixing, flocculation and sedimentation tanks, etc. The costs vary widely depending on the individual situation. These facilities are installed for general water purification requirements such as turbidity removal from surface water supplies. Using these facilities for fluoride removal therefore saves the capital investment on equipment specially designed for this purpose.

The chemical cost comprises a major portion of the total fluoride removal cost. Small quantity prices can cost 50 % more than bulk handling of chemicals. The cost basically is the additional cost of alum required to bring about a satisfactory reduction of fluorides, an amount in excess of that for normal treatment. This obviously depends on the amount of fluorides to be removed. Other components of the chemical cost are the costs for pH adjustment (e.g. lime) and possibly coagulant aids. Because of sludge production, the chemical cost is also closely associated with the disposal cost.

3.1.1.8 Case Studies

Pilot plant results using alum coagulation to remove fluorides have been reported (Maier 1947). In Great Falls, Md., with the conventional type of plant, fluoride was reduced in two steps from 6 to 3.5 mg/L and from 3.5 to 1.0 mg/L. Each step required 100 mg/L alum, 100 mg/L clay and 25 mg/L lime. With these same dosages, a sludge-blanket type plant in Cincinnati removed about 25 % more fluoride.

A plant was proposed in La Crosse, Kansas to treat the high-fluoride water supply by alum coagulation (Culp and Stoltenberg 1958). A fluoride reduction from 3.6 mg/L to either 1.5 mg/L or 1.0 mg/L was sought. An alum dose of 225 or 315 mg/L would have been required depending on the final fluoride level chosen. Provisions were proposed for incremental feeding at various points in the rapid-mix and flocculation basins. Chlorine addition rather than

aeration was proposed for iron removal. Rapid mixing for 1 to 2 minutes followed by 30 minutes of flocculation would have been provided. Lime addition at 15 to 20 mg/L in the last section of the flocculation basin was proposed. Sedimentation with 2 to 4 hour detention was to be followed by gravity, rapid sand filtration. Sludge ponding, preferably in an overflow lagoon, would have been provided for alum sludge disposal. When a new low-fluoride water source became available for blending with the existing source, the plant could then be fully used to treat the combined supply for softening and removal of iron and manganese.

3.1.1.9 Advantages

1. Among many materials tested as coagulants or adsorbents for fluoride removal during the coagulation process, only alum has been found practical for full-scale plants.
2. Alum has relatively high fluoride removal capacity, in the absence of interferences and at favourable pH's.
3. Alum coagulation can also reduce iron, manganese, colour and turbidity. Iron and manganese are removed in the process by addition of chlorine.
4. Soft water is ideally suited to fluoride reduction by alum coagulation.
5. Alum is readily available and relatively inexpensive.
6. Waste disposal is not a problem if alum sludge can be satisfactorily handled in an overflow lagoon.
7. Alum coagulation has been widely used in conventional water treatment. Therefore equipment, chemicals and operating procedures are comparable to those in conventional treatment plants and require little special training for local employees, making the defluoridation process within reach of smaller communities.
8. A plant treating the existing water supply by alum coagulation may be easily adapted to treatment of water from other future sources.

3.1.1.10 Disadvantages

1. Large doses of alum in excess of those required for turbidity and colour removal are often required, resulting in high chemical and sludge disposal costs.
2. A high alum dosage can also raise the sulphate content to an undesirable level.
3. The process requires sludge collection, dewatering and disposal, and long start-up and shut-down periods.

4. Highly mineralized groundwaters with excessive fluorides will limit the effectiveness of alum in removing fluorides. Alkalinity will also interfere with fluoride removal.
5. Although one study showed that calcium actually improved fluoride removal slightly in alum coagulation, other reports generally suggested that hardness in water may interfere with fluoride removal.
6. Careful pH control is necessary to optimize treatment. Re-adjustment is also required before the treated water can be distributed.
7. Alum coagulation is not readily adaptable to very small water systems or individual wells operating on demand. This process is unreliable and impractical for home application.

3.1.2 Lime Softening

3.1.2.1 Principle

There are two ways in which lime can remove aqueous fluorides. When the fluoride concentration is high, exceeding 20 mg/L, excess lime may be added to the water to precipitate calcium fluoride which is slightly soluble (Parker and Fong 1975). With this removal mechanism, the best achieveable residual concentration is 8 to 10 mg/L of fluoride ion, corresponding to the solubility limit of calcium fluoride. Therefore, this kind of lime treatment only applies to preliminary treatment of industrial wastewaters containing high levels of fluorides. However, it may also be useful in disposing the fluoride concentrates generated by other methods used for defluoridating drinking waters.

The removal of fluorides from water supplies during the lime softening process is the result of a different mechanism. In the softening process, the lime removes magnesium hardness by precipitating magnesium hydroxide. A portion of the fluorides present is adsorbed by the gelatinuous magnesium hydroxide precipitate and co-precipitates with it. Scott *et al.* (1937) have developed a formula from experimental observations, relating the efficiency of fluoride removal to the amount of magnesium removed:

$$F = F_0 - (0.07F_0)(Mg^{0.5}) \quad (1)$$

where,

F = residual fluoride concentration (mg/L)

F_0 = initial fluoride concentration (mg/L)

Mg = magnesium removed (mg/L as Mg^{2+})

This relation seemed to hold for initial fluoride concentrations from 1.5 to 3.5 mg/L. A graphic presentation of the formula is given in Figure 9.

In order to secure a desirable amount of fluoride reduction, sufficient magnesium must be available for removal in the first place. According to the formula, reduction of the fluoride content from 3.3 to 1.0 mg/L would require a magnesium removal of 100 mg/L. Such a high magnesium concentration is rare in natural waters and magnesium compounds would have to be supplemented to insure adequate removal of fluorides by this method.

The calcium hardness in water may also play a role in magnesium flocculation. The results of Sollo *et al.*'s work (1978) showed that calcium improved the texture and settleability of the floc.

3.1.2.2 Operation

Large amounts of chemicals are required for this process. The lime dosage may be calculated in the same manner as in a normal water softening problem and must correspond to the total quantity of magnesium originally present and added, and the necessary caustic alkalinity. Nearly complete precipitation of magnesium needs a pH greater than 11. Sufficient lime is required to raise the pH to at least 10.5 for a high percentage of magnesium removal. The necessary caustic alkalinity is about 30 mg/L.

Magnesium may be added to magnesium-deficient waters in the form of dolomitic lime (CaO and MgO), magnesia (MgO), or magnesium sulphate (Maier 1953). When magnesia is used in waters containing sodium fluoride, the magnesia is thought to become partially hydrated, then magnesium fluoride and sodium hydroxide are formed by metathesis, and finally the magnesium fluoride is combined with the magnesia, perhaps forming an oxyfluoride (Maier 1947, 1953).

Carbon dioxide is required for pre- and recarbonation. Pre-carbonation is necessary to convert the magnesia to magnesium carbonate. Recarbonation is used to neutralize the high pH effluent. Carbon dioxide for pre-carbonation may be applied as a gas, or it may be produced from conversion of bicarbonates by contacting the water with a source of hydrogen ions (Maier 1947).

The usefulness of coagulant aids in magnesium flocculation for removing fluorides was studied by Sollo *et al.* (1978). Anionic polyelectrolytes improved settleability of the floc while the nonionic type did not.

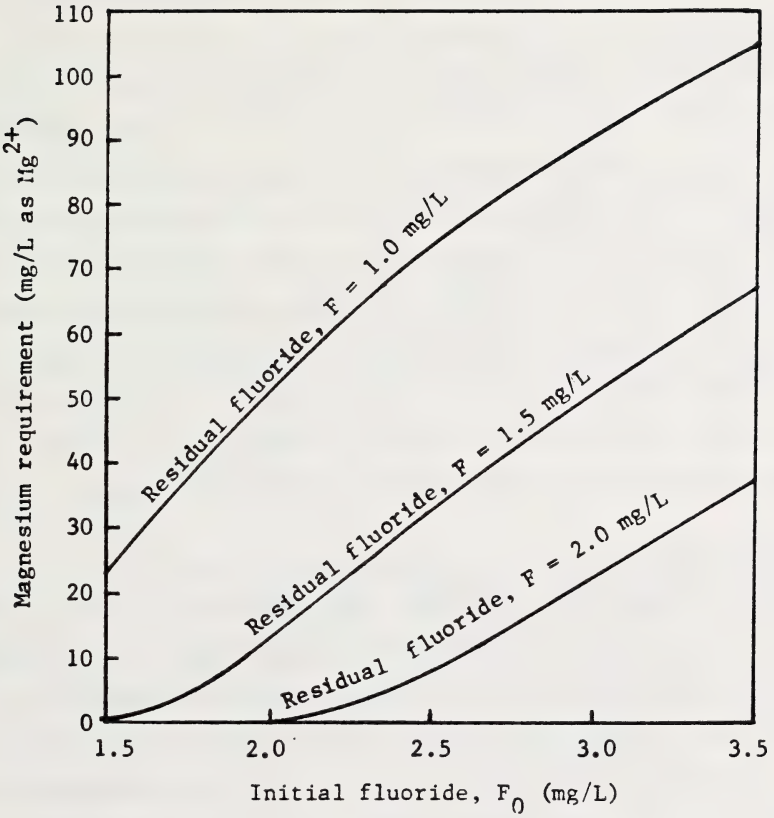


Figure 9. Magnesium requirements for fluoride removal in lime-softening (derived from Scott *et al.* 1937)

An ordinary lime or lime-soda softening plant of standard design is adequate for fluoride removal application. The design will comprise dissolvers, reaction and sedimentation tanks and filters, with provisions for carbonation. Initial operation will require skilled technical supervision to adjust the applied chemicals. Periodic checks are sufficient once proper dosages have been established.

3.1.2.3 Costs

Lime softening is normally done in the coagulation process, using the same facilities plus some additional feeding and carbonation equipment. Like the alum coagulation method, fluoride removal by the softening process has the advantage of conventional treatment facilities and saves the capital investment on special equipment. The operating cost consists of the normal cost for water softening plus any additional chemical and disposal costs attributable to further reduction of the residual fluoride to the proper level. Labour cost is not expected to exceed that for the ordinary softening operation. The additional chemical costs are those of added magnesium compounds and excess lime, and depend on the fluoride and magnesium levels in the raw water. Under low-fluoride and high-hardness conditions, most of the treatment cost may be shared between the removal of the two parameters.

3.1.2.4 Case Study

A lime softening plant at Bloomdale, Ohio, operating at 379,000 L/d, reduced the fluoride from 2.2 to 1.2 mg/L without the need of adding magnesium to the water (Finkbeiner 1938). Magnesium was reduced from 98 to 52 mg/L (assumed to be mg/L as Mg^{2+}). The degree of fluoride removal agreed closely with the formula developed by Scott *et al.* Lime in the amount of 223 mg/L (as CaO) was fed to achieve these results. An increased dosage could have resulted in more fluoride being removed along with a greater magnesium reduction. The equipment set-up of this plant was described in Finkbeiner's report.

3.1.2.5 Advantages

1. With water softening and partial fluoride removal combined in one process, this is particularly suitable for treating hard waters that contain relatively low levels of fluorides, up to about 3.0 mg/L.
2. The same equipment and treatment chemicals are used for the combined functions. If a proper reduction of fluorides can be achieved with the natural magnesium hardness

present, no more chemicals are required other than the amounts needed for softening. In this case, the plant would be operating at the normal cost of softening alone.

3. The operation is identical to that for ordinary softening plants with no greater technical requirements.

3.1.2.6 Disadvantages

1. The method is attractive only when water softening is also required. A plant using this process to specifically remove fluorides is not economically practical. Application is therefore limited.
2. The chemical and sludge handling costs are typically high. In situations where high levels of fluorides are present and large quantities of magnesium must be added, the chemical costs would become excessive, rendering this process impractical on a plant scale.
3. Like all other coagulation/precipitation methods, this process is not suitable for systems operating on demand. Sludge problems and long start-up and shut-down periods are expected.

3.1.3 Other Chemicals

A number of coagulants other than alum have been tried for fluoride removal (Boruff 1934; Hung 1981; McKee and Johnston 1934; Sollo *et al.* 1978). These include sodium aluminate, sodium silicate, ferric salts, calcium hydroxide phosphate, bentonite, etc. Hung found calcium hydroxide phosphate, $Ca_{10}(OH)_2(PO_4)_6$, moderately effective but a large dosage was required. All other coagulants have been shown practically ineffective.

Another fluoride removal method that can be accomplished in the mixing and sedimentation basins of conventional treatment involves the formation of a fluorapatite precipitate. It requires the addition of phosphate and calcium to precipitate tricalcium phosphate, $Ca_3(PO_4)_2$, which then complexes with fluorides to form fluorapatite. Phosphoric acid and lime are used for this purpose. Early investigations on this process were done by Adler *et al.* (1938); and by MacIntire and Hammond (1938) who tried various commerical forms of powdered tricalcium phosphate. Adler *et al.* indicated that 6 g of fluoride would be removed per 1 kg of tricalcium phosphate when the pH was controlled at 7 to 7.5. A more recent study by Sollo *et al.* (1978) showed that 190 mg/L PO_4^{3-} was required for 50 % fluoride reduction when 5

mg/L was originally present. They also found that lime must be added to give a pH level of at least 10.5 in order to maintain a low residual phosphate concentration. At elevated pH, fluoride removal was also improved as a result of magnesium precipitation.

A modification to this fluorapatite precipitation method is known as the Andco process in which calcium chloride is used initially, and lime is later added for pH adjustment. The overall equation is as follows (O'Brien 1983):

$$F^- + 3H_3PO_4 + {}^1/_2CaCl_2 + 4{}^1/_2Ca(OH)_2 \leftrightarrow Ca_5(PO_4)_3F + Cl^- + 9H_2O$$

Commercial package plants are available from Andco Environment Processes, Inc. The operating cost has been reported at $2.20/kg F^- removed (Rigdon 1980). There are additional costs for sludge disposal, polyelectrolyte and pH adjustment. The insolubility of fluorapatite provides a favourable condition for disposal of the sludge. However, because of high sludge production, sludge handling can be a problem.

Sollo *et al.* (1978) combined alum coagulation and fluorapatite preciptation in a single flocculation-sedimentation step and found that unless the alum flocs had been removed before fluorapatite formation, the results were not as good as those achieved by sequential application of individual processes. This can be explained by the amphoteric nature of aluminum hydroxide and its re-entrance into solution at higher pH's.

All coagulation and precipitation methods have the major drawbacks of high chemical requirements and high sludge production. Other additive methods involving the use of certain adsorbents in the powdered form have been investigated (Hung 1981; MacIntire and Hammond 1938; Sollo *et al.* 1978). These adsorbents include bone char, tricalcium phosphate, activated alumina, activated carbon, etc. However, these adsorbents are more practical to use in contact filters. Such applications are reviewed in the following sections.

3.2 ION EXCHANGE/ADSORPTION METHODS

3.2.1 General

The defluoridation processes reviewed in the following sections involve passage of the water through a contact bed where the fluoride ion is removed by ion exchange and/or adsorption. Various materials have been studied for their potential as defluoridating media. Only bone char, synthetic bone and activated alumina have been successfully employed in

municipal water treatment plants to specifically remove fluorides. Synthetic ion exchange resins are used to remove fluorides along with other common ions.

At the start of the treatment cycle, the effluent fluoride content will drop rapidly to a low level. When the bed capacity becomes exhausted, breakthrough will occur and the residual fluoride concentration will rise. The treatment cycle ends when the residual fluoride concentration averaged over the entire period of treatment reaches the desirable level.

Obviously, the actual fluoride content in the effluent varies above and below the desirable level during the treatment run. Dangel (1977) believed that the fluoride concentration should be controlled for short averaging periods because tooth enamel formation may be affected by short term perturbations. The average cycle lengths of 5.5 and 8 days at the plants in Britton, South Dakota and Bartlett, Texas, respectively, appeared to be a reasonable time span. Samples are preferably analysed daily for the averaging procedure.

The defluoridating media are normally regenerated to restore the defluoridating capacity after each use. In general, replacement is economically feasible only in the smaller units. In some processes, eventual replacement of the media is inevitable because of a gradual capacity loss through successive regeneration.

Regeneration of bone materials and activated alumina generally begins with a cycle backwash. The backwash is required to remove any filtered suspended solids and to loosen over-packed beds (in case of downflow treatment), breaking the tendency towards wall effects or channeling. The backwash rate should be carefully adjusted to ensure proper cleaning while avoiding upsetting and washing out of the bed. Sudden shocks to the bed can result in channeling or short-circuiting of the water. The backwash is followed by a caustic treatment to remove the accumulated fluoride and restore the defluoridating capacity of the media. Caustic soda (NaOH) is universally used for this purpose. A subsequent caustic rinse then removes excess caustic from the unit. The rinse water is preferably used as long as it remains effective before a neutralizing agent is applied. Phosphoric acid, sulphuric acid, carbon dioxide, hydrochloric acid and sodium disulphate have been used as an acidifying agent. Finally, a fresh water rinse prepares the bed for the next treatment cycle. Too high a rinse rate will induce a packing of the bed while too low a rate will result in low productivity of the overall operation. Theoretically, at 100 % regeneration efficiency, all the fluoride removed in the run preceding the regeneration can be accounted for in the regeneration washings with a peak fluoride

concentration that occurs during the caustic rinse. To maintain a continuous output of the treated water, two units may be installed to operate alternately, or in parallel with staggered regeneration periods.

Operation for these processes normally does not require excessive labour time. Most labour is used during the regeneration process (Harmon and Kalichman 1965). Disposal of large volumes of concentrated regeneration wastes is a common problem for these methods. Evaporation ponds used for disposal must be impervious in order to protect the groundwater.

The choice of media or processes should be based on their relative effectiveness, fluoride removal capacity and selectivity for the fluoride ion. These factors can be determined by experimental studies. The selection should also consider factors such as the ease and efficiency of bed regeneration, rates of attrition and capacity losses of the media, as well as initial and operating costs.

3.2.2 Bone

Bone is known to have an affinity for fluorides, probably due to the anion exchange properties of apatites which are essentially calcium phosphate minerals in the form of $n[Ca_3(PO_4)_2]\bullet CO_3$ (Smith and Smith 1937). The fluoride ion may replace the carbonate radical and form an insoluble fluorapatite. Upon regeneration with a caustic solution, the accumulated fluoride is removed and the fluorapatite becomes hydroxy-apatite. This is the form suitable for treatment with the fluoride ion replacing the hydroxy radical.

In the earliest bone contact method suggested (Smith and Smith 1937), the bone was prepared by degreasing in boiling water. It was then crushed and boiled in a dilute sodium hydroxide solution. The caustic was rinsed and neutralized by hydrochloric acid. Finally, the material was washed, dried and graded. The regeneration procedure involved the same sodium hydroxide treatment, washing and neutralization as in initial preparation.

In jar tests reported by Smith and Smith, 2 g of bone prepared in this way reduced the fluoride concentration in 500 ml of water from 6.0 mg/L to 0.8 mg/L. A dose of 0.5 g achieved the same residual level when the original fluoride concentration was only 2.0 mg/L. A slight increase in the phosphate ion was noticed in the effluent but this was considered beneficial. The results of using different mesh sizes indicated that finer bone provided more contact surface and improved removal. For filter application, however, there is a practical limit for fineness as

governed by the loading rate. The study also showed that longer contact times resulted in more complete adsorption of fluorides.

A gravity bone filter consisted of 2.27 kg of bone in an aspirator bottle was later field tested at a 1.89 L/min loading rate. The filter had a maximum efficiency of reducing the fluoride content from the original 3.5 mg/L to a residual level of 0.1 mg/L. The capacity was still not exhausted when the test terminated at 530 L of water passage.

Smith and Smith suggested that this bone treatment was practical for home use in a faucet filter. However, there have been reports of objections to the taste of water treated by these home filters (Maier 1947, 1953, 1971). The cost of regeneration would also be prohibitively high for use on a municipal scale. These limitations have led to the development of more suitable bone materials.

3.2.3 Synthetic Bone

The synthetic bone material is a mixture of tricalcium phosphate, $Ca_3(PO_4)_2 \bullet H_2O$, and hydroxy-apatite, $3Ca_3(PO_4)_2 \bullet Ca(OH)_2$, specially prepared by reacting phosphoric acid with solutions of lime (Adler *et al.* 1938). Tricalcium phosphate precipitate is known to be gelatinous. When dried, it develops a porous structure ideal for adsorption. The physical properties and composition of synthetic bone therefore suggest that fluorides are removed by adsorption along with the formation of a fluorapatite. A caustic regeneration will restore the material to the original hydroxyl form, again available for exchange with the fluoride ion.

Although synthetic bone is available in a powdered form for use as an additive in water treatment, it is more practically used in the granular form as a contact filter. The material is highly insoluble in water and has a density compatible with backwash requirements (Behrman and Gustafson 1938). Reported fluoride removal capacities of synthetic bone are given in Table 4. These capacities were based on a breakthrough point where the fluoride content in the effluent had risen to 1 mg/L.

3.2.3.1 Operating Conditions

Lower flow rates generally favour fluoride removal. It may be particularly desirable to use a lower rate for waters having a high concentration of fluorides or interfering chemicals. The maximum rate of flow that can pass through the media depends on the grain size of the

Table 4. Fluoride removal capacities of synthetic bone

REFERENCE	CAPACITY*	TEST CONDITIONS
Alder *et al.* 1938	±3.7 g/kg	- 20 to 40 mesh - both synthetic and natural (soft) waters - varied initial fluoride levels - virgin bed, without prior regeneration
Behrman and Gustafson 1938	660 g/m³ (76,900 L/m³ per cycle, removing 8.6 mg F^-/L avg.)	- 20 to 40 mesh - synthetic water - initial fluoride 10 mg/L - initial capacity was not diminished when CO_2 was used as neutralization agent - flow rate 41 L/min/m²
Goodwin and Litton 1941	629 g/m³ rated (based on synthetic water) 609 g/m³ actual	- natural water - sulphate 149 mg/L - initial fluoride 5.2 mg/L - initial capacity was not diminished when 16 kg caustic per m³ bed was used in regeneration - flow rate 41 L/min/m² per 250 mm depth
Maier 1947	686 g/m³ rated	

* the quantity of fluoride removed per quantity of bone before the effluent exceeds 1 mg F^-/L

media which in turn influences the capacity of the bed. For a given flow rate, the adsorption capacity is lower for coarser material. The rate of flow through the coarser material must be reduced in order to achieve comparable results as a finer material (Adler *et al.* 1938).

A flow rate of 40.74 L/min/m^2 bed area per 250 mm of bed depth is considered optimum (Goodwin and Litton 1941). While a lower rate will not increase the removal capacity appreciably, the capacity will drop considerably at higher rates. Excessive flow rates have a crushing effect on synthetic bone material and may result in loss of media through the treated water (Harmon and Kalichman 1965).

Different observations between natural and synthetic waters in response to treatment have suggested that fluoride removal may be influenced by the water chemistry (Goodwin and Litton 1941). Adler *et al.* (1938) observed better removal of fluorides with soft waters than with hard waters. However, they did not find any effects of the influent fluoride concentration or pH on the removal capacity. Certain substances are known to interfere with fluoride removal. For every 100 mg/L of sulphate, the removal capacity decreases about 3 %. The iron content, if exceeding 0.1 mg/L, will also clog the filter (Maier 1947).

3.2.3.2 Regeneration

The exhausted bed may be treated with a 1 % sodium hydroxide solution to remove the accumulated fluoride. About 16 kg of caustic soda is required per m^3 of media for a satisfactory restoration of the bed capacity (Goodwin and Litton 1941). Complete restoration of the bed capacity is not possible if hydrochloric acid is used as the neutralizing agent. With HCl, there is a reported 2.5 to 3.0 % loss of media per regeneration (Adler *et al.* 1938). Even with continuous make-up for this loss, the capacity will continue to decrease after each regeneration until it is permanently diminished. The regenerated bed using HCl for neutralization shows increased bulk density, reduced porosity and larger particle size (Behrman and Gustafson 1938).

Carbon dioxide would be a better neutralizing agent. The use of CO_2 did not result in loss of media or fluoride removal capacity through successive regeneration when investigated by Behrman and Gustafson (1938). The preservation of original density, porosity and particle size of the media indicated that constant hydraulic operating conditions may be maintained. The media may, however, still be subject to an imperceptible attrition loss. Goodwin and Litton (1941) estimated a loss of 5 % per 300 cycles.

3.2.3.3 Case Studies

Synthetic bone was the first material commercially available for defluoridation. The first full-scale application was at Climax, Colorado, from 1937 to 1949 (Wamsley and Jones 1947). There were four gravity-type defluoridation units operating in parallel with a maximum combined capacity of about 1.14 ML/d. The units were preceded by coagulation, softening, sedimentation, filtration and recarbonation processes. Each defluoridation unit was a 2.6 m diameter by 3.0 m high tank of redwood construction containing 1.14 m of media. When one unit was out of service (e.g. for regeneration), automatic controls allowed the load to be taken by the remaining units. One or two units would require regeneration each day, taking about 3 hours per unit. The regeneration solutions and rinse waters were gravity-fed by the same distribution system. The 1 % caustic solution was returned to the solution tank after use. The CO_2 used for neutralization was derived from dry ice and diffused in solution by carbonators. The influent fluoride concentration fluctuated between 2 and 14 mg/L, and was reduced to an average of 0.6 mg/L in the effluent. The operating cost for the fluoride removal treatment was about $40 to $60 /ML, accounting for 60 % of the cost of operating the entire plant. This was considered a plant of high complexity at that time and therefore the cost was extraordinarily high.

A similar fluoride removal process was adopted in a plant at Britton, South Dakota, in 1948. Excessive losses of the synthetic bone material through attrition, reaching 52 % per year, forced the plant to replace the synthetic bone with bone char which later proved to be a much better defluoridating medium.

3.2.3.4 Advantages

1. Synthetic bone material appears to be highly efficient in removing fluorides, capable of reducing the fluoride content in water to near zero.
2. The physical properties (porosity, insolubility in natural water of normal pH and alkalinity) of synthetic bone are characteristic of an effective adsorbent.
3. The exhausted media can be economically regenerated for repetitive application in municipal plants.

3.2.3.5 Disadvantages

1. The material is friable with excessive attrition loss reported in actual installations. Consequently, frequent replacement is necessary.
2. Sulphate ion will affect fluoride removal quite significantly.

3.2.4 Bone Char

Bone char, also called animal charcoal or bone black, is ground animal bones charred to remove all organics. It is essentially a tricalcium phosphate and carbon mixture, originally developed for the sugar refining industry. This porous and amorphous solid has high physical stability. When first investigated by Burwell *et al.* (1945), it showed a fluoride adsorption capacity exceeding that of synthetic bone. A capacity reaching 2,900 g fluoride per m^3 bone char was reported at the Britton plant, removing an average of 5 mg/L fluoride.

3.2.4.1 Operating Conditions

The influent pH must be carefully controlled when using bone char as a defluoridating medium. Ideally, the pH should be kept as low as the media can tolerate without dissolution because it has been shown that the fluoride removal capacity of bone char is greater at lower pH's (Maier 1971). Much earlier, Burwell *et al.* (1945) discovered the influence of bicarbonates on fluoride removal and suggested pH adjustment on high alkaline waters. Their report also indicated that fluoride removal may be influenced by the presence of dissolved and suspended solids, the size granulation of the bone and the water flow rate. The treatment system design must allow an ample leeway for fluctuations of these factors. A flow rate of 1.67 L/hr per kg of filter was proposed for the design purpose. Burwell *et al.* also suggested that silt and organic matter be removed by preliminary filtration.

Bone char also has a considerable capacity for arsenic adsorption, even greater than that for fluoride. The accumulated arsenic cannot be recovered from the media. According to Bellack (1971), if arsenic is also present in the water, arsenic adsorption will result in an irreversible chemical change of the bone char structure, adversely affecting fluoride removal as well as further arsenic removal.

3.2.4.2 Regeneration

Burwell *et al.* (1945) discovered that bone char could be more efficiently regenerated by trisodium phosphate and monosodium phosphate than by the caustic soda - carbon dioxide method generally used for synthetic bone. The proposed reagents are non-corrosive, safe and easy to handle, making them more suitable for small installations. However, the phosphate reagents cost more than the conventional reagents. More satisfactory regeneration could be obtained for bone char than for synthetic bone under identical conditions. Nevertheless, Burwell *et al.* suggested that replacement of the exhausted bed would be more practical for smaller installations.

In municipal installations, discarding the exhausted filter material would not be economically feasible. The caustic soda - carbon dioxide regeneration method was successfully employed in the Britton plant which had replaced synthetic bone with bone char (Maier 1953, 1960, 1971). The carbon dioxide was later replaced by sulphuric acid. In Southern California (Harmon and Kalichman 1965), household units and small installations (11 L/min per unit) did not employ regeneration. Two larger installations at 125 L/min and 135 L/min per unit used caustic soda - phosphoric acid and caustic soda - sodium bisulphate, respectively, for regeneration. If arsenic is present, bone char can only be used on a non-regeneration basis.

3.2.4.3 Design Criteria for Small Installations

Burwell *et al.* (1945) suggested some possibilities of using bone char in defluoridating water for homes, schools, and smaller communities. In the simplest arrangement, a 19 L glass bottle may be used as a filter unit while another connecting 19 L glass bottle may be used as a raw water reservoir. The exhausted bed will be discarded for such an installation. Because this system is limited to fluoride removal, the feedwater must be acceptable for drinking water in all other respects and there must be no chemicals that will interfere with the removal of fluorides. The size and capacity of the system should be based on at least the maximum daily consumption expected. Some margin of safety should be allowed for emergency situations. A flow rate of 1.67 L/hr per kg of media is recommended to allow a proper contact time with the media. The depth and particle size of the media may affect the flow rate chosen. While the system is operating, periodic tests are required to determine when the bed needs to be replaced. A simplified test procedure has been developed by Burwell *et al.* and is applicable for small consumers.

3.2.4.4 Costs

Land requirement and capital cost for bone char defluoridation plants are expected to be comparable to those for standard ion exchange plants. Replacement cost of media can be quite significant for bone char which tends to degrade to some extent. The material is fairly expensive, costing about $1,700/m^3 in 1978 dollars (Sorg 1978). The major operating cost item is regeneration, a process which involves most of the chemical and labour requirements. The unit cost of treatment therefore depends on the productivity of water between regenerations, which in turn depends on the raw water fluoride level and the bed size. The bed size, which is a function of capital cost, must be properly balanced with the water productivity in order to develop an economical design of the system. Actual bone char treatment cost based on operating experience is scarce. Cost curves developed by Watson *et al.* (1974) on the basis of data at Britton are shown in Figures 10 and 11.

3.2.4.5 Case Study

The plant in Britton, after replacing the original synthetic bone with bone char, operated from 1953 to 1971. In the process, this plant became probably the best-known and most successful defluoridation plant in United States using this material (Maier 1960, 1971). The equipment and regeneration procedure were essentially unchanged from those originally adopted for synthetic bone. The relevant plant data have been reported as:

fluoride removal	- from 6.7 mg/L to an equivalent of 1.5 mg/L
flow rate	- varied, 144 to 780 L/min
productivity	- 1.7 ML treated water/cycle (initial operation)
	- 4.7 ML treated water/cycle (after lowering pH of raw water to 7.1)
cycle lengths	- 3 days, summer (final)
	- 7 to 8 days, winter (final)
media	- 8.5 m^3 of 28 to 48 mesh bone char on 300 mm of graded gravel
bed capacity	- 1,030 g fluoride/m^3 (initial operation)
	- 2,900 g fluoride/m^3 (after lowering pH of raw water)
equipment	- 2.74 m dia. by 3.05 m high pressurized contact tank of heavy steel construction, equipped with steel pipe-grid underdrain and cast iron caustic distributor

- 2.74 m dia. by 2.74 m high caustic soda dilution tank equipped with electric motor-driven mixer and pump
- CO_2 liquefiers, later replaced by sulphuric acid dilution apparatus

backwash - 1,400 L/min of treated water (from storage) for 18 min

caustic treatment - 18,900 L of 1 % caustic soda solution (prepared by reusing 15,100 L of rinse water along with 3,800 L of well water), requiring about 25 min of passage

caustic rinse - 26,500 L of raw water at 568 L/min

neutralization - weak CO_2 solution prepared with 38 kg CO_2 gas (from liquefied dry ice) diffused in 32,200 L raw water (568 L/min)
- 0.05 N H_2SO_4 solution, also used in pH adjustment of raw water, later replacing CO_2

costs - equipment $12,245 (1947, including the synthetic bone as media)
- bone char media $540/bed (1960)
- chemicals

$14/ML (1960)

$5/ML (1971, based on extended cycles, using H_2SO_4 in regeneration and in lowering pH of raw water)

The mesh size of 28 to 48 was selected as a compromise between fluoride removal efficiency and head loss in the pressure tank. Carbon dioxide was replaced by sulphuric acid in regeneration after the latter was found cheaper, easier to handle and just as effective. The plant data indicate that lowering the pH of the influent will dramatically increase the capacity of bone char. Consequently, regeneration frequency is reduced, reducing the overall chemical cost. To avoid dissolution of the media in acids, the influent pH was limited to 7.1 at Britton although even better removals were expected at lower values. The sulphuric acid dilution system was used to provide convenient, continuous acid feed to the raw water.

3.2.4.6 Advantages

1. The high porosity of bone char favours fluoride adsorption. Physical stability appears to result in low loss of media from attrition (Burwell *et al.* 1945)
2. Odour and taste may also be removed by bone char, probably because of adsorption by the carbon (Burwell *et al.* 1945).
3. Bone char has been shown superior over synthetic bone in terms of greater fluoride

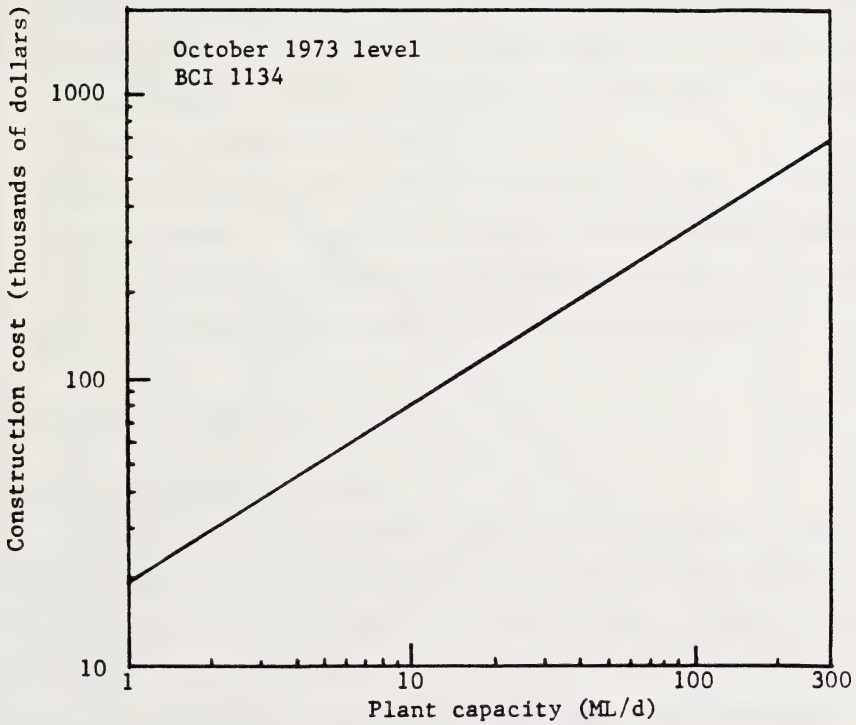


Figure 10. Construction cost for bone char defluoridation plants (Watson *et al.* 1974)

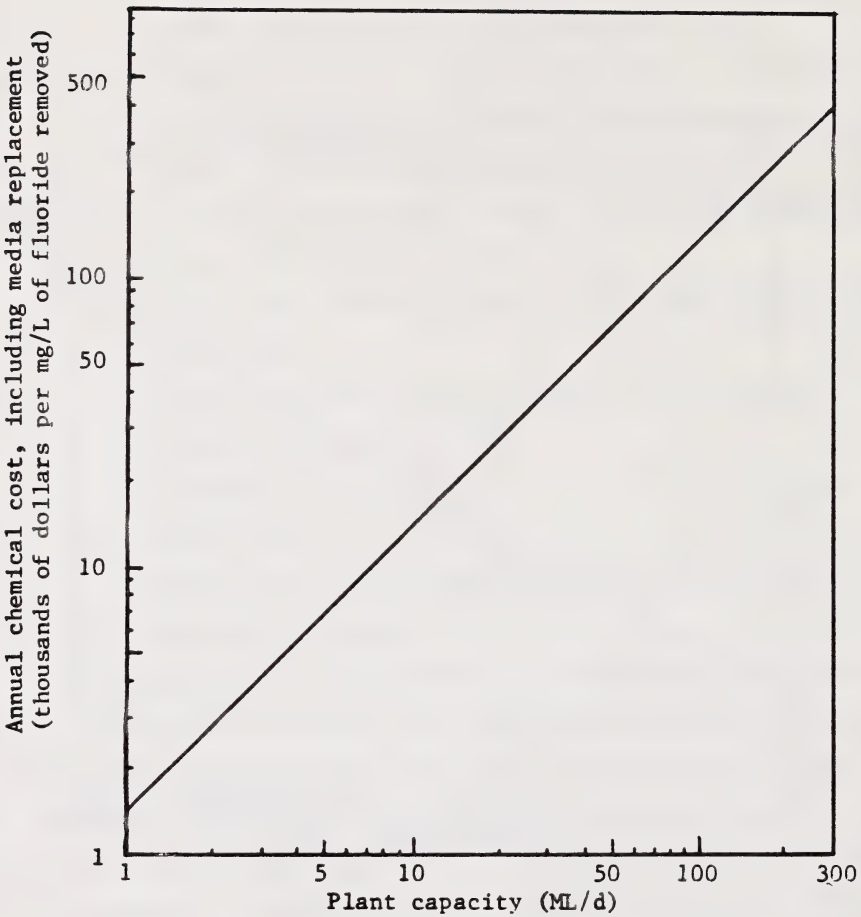


Figure 11. Chemical and media replacement costs for bone char defluoridation (Watson *et al.* 1974)

removal capacity, lower cost, more efficient regeneration and lower attrition loss.

4. The method is adaptable to small communities, camps, schools and homes where the exhausted bed is discarded.

3.2.4.7 Disadvantages

1. Despite better regeneration efficiency than for synthetic bone, there is still a 12 % reduction in capacity after the first regeneration of bone char (Burwell *et al.* 1945).
2. The use of bone char has not been too successful in certain plants (Harmon and Kalichman 1965), with excessive degradation of the media and rapid decreases in removal capacity and in productivity of treated water reported.
3. Apparently, successful use of bone char for defluoridation requires careful control of the operating conditions. For example, the media will dissolve under acidic condiditon.
4. Bone char would not be practical for fluoride-bearing waters that also contain arsenic.
5. Regeneration of bone char usually can only be handled in larger installations.

3.2.5 Activated Alumina

3.2.5.1 Physiochemical Properties

Activated alumina is the common name for gamma aluminum oxide (γ-Al_2O_3), a porous compound having a typical BET (Braunauer, Emmett, Teller) surface area of 150 to 300 m^2/g (Singh and Clifford 1981). It is prepared by lower temperature dehydration of hydrous aluminum oxides at 300 to 700 °C, not to be confused with the high temperature α-Al_2O_3. Alumina has been recognized as an adsorbent for organic and inorganic compounds and used in a variety of processes.

Activated alumina is considered a polar adsorbent, containing cation lattice discontinuities that give rise to localized areas of negative charge with balancing areas of positive charge (Umland 1956, cited by Clifford *et al.* 1978). Both cationic and anionic adsorption sites are available. In aqueous solution, the net surface charge of activated alumina will determine whether cations or anions will be predominantly adsorbed or exchanged onto the surface. Under certain conditions, non-ionic species can also be adsorbed (Clifford 1982). The sign of the surface charge depends on the pH of the solution relative to the isoelectric point of the alumina. The isoelectric point of activated alumina shifts with different pretreatments,

probably due to hydration (Choi and Chen 1979). It is also affected by structural and adsorbed impurities of the adsorbent (Parker 1965, cited by Choi and Chen 1979).

Activated alumina is an amphoteric compound known to have centres of acidic and basic character, as well as centres with either oxidizing or reducing properties (Ponec *et al.* 1974, cited by Choi and Chen 1979). Commercial grade activated alumina is in the basic form and acts as a cationic adsorbent. In its acid-treated form, it becomes an anion exchanger with fluoride being one of the most preferred ions in the selectivity sequence:

$$OH^- > F^- > SO_4^{2-} > Cl^- > HCO_3^- \qquad \text{(Singh and Clifford 1981)}$$

For use as an anion exchanger, the activated alumina may be pretreated with acid, or the feed water may be acidified before treatment.

3.2.5.2 Fluoride Removal Mechanism

The physiochemical properties of activated alumina dictate that fluoride ion may be specifically removed by molecular sorption when the surface charge of the alumina is positive, and anionic adsorption behavior prevails. Such a condition exists in acid medium. However, surface charge may not be the only factor responsible for ion removal. Savinelli and Black (1958) found evidence of an ion exchange mechanism for fluoride removal even on a neutral surface. Specific adsorption (by combined ionic and nonionic bonding) can occur even when the surface is not charged. Adsorption can also arise from electrostatic attraction augmented by hydrogen bonding, coordinate bonding, or Van der Waals forces (Singh and Clifford 1981). Another possible mechanism is the precipitation of sparingly soluble bases or basic salts (Umland 1959, cited by Singh and Clifford 1981).

Clifford *et al.* (1978) have developed a simplified theory for the adsorption/ion exchange process. When basic alumina, alumina•HOH, is treated with acid, e.g. HCl, acidic alumina is formed:

$$\text{alumina•HOH} + HCl \rightarrow \text{alumina•HCl} + HOH$$

In this acidic form, the chloride ion can be readily displaced by the more preferred fluoride ion providing the feed solution is slightly acidic to preclude hydroxide ion competition:

$$\text{alumina•HCl} + NaF \rightarrow \text{alumina•HF} + NaCl$$

The fluoride-bearing alumina may be regenerated by a dilute solution of hydroxide which displaces fluoride:

$$\text{alumina•HF} + 2NaOH \rightarrow \text{alumina•NaOH} + NaF + H_2O$$

The regenerated form must again be acidified to restore the fluoride removal capacity:

$$\text{alumina}\bullet\text{NaOH} + 2\text{HCl} \rightarrow \text{alumina}\bullet\text{HCl} + \text{NaCl} + \text{HOH}$$

3.2.5.3 Kinetics of Fluoride Removal

Wu and Itemakin (1979) have developed a mathematical model to describe the kinetics of fluoride removal by activated alumina. The kinetic expression of the removal process is in the following general form:

$$r = k_1F_1^x - k_2F_2^y \quad (2)$$

where,

r = overall rate of fluoride removal (mg/g/min)

k_1, k_2 = forward and reverse reaction rate constants, respectively

$F_1 = (F_0 + F) / 2$, the average liquid-phase fluoride concentration (mg/L)

F_0 = influent fluoride concentration (mg/L)

F = time-dependent effluent fluoride concentration (mg/L)

F_2 = solid-phase fluoride concentration, i.e. the amount of fluoride adsorbed per unit mass of alumina (mg/g)

x, y = exponents

The overall rate may also be expressed as follows:

$$r = (Q / m)(F_0 - F) \quad (3)$$

where,

Q = volumetric flow rate (L/min)

m = mass of activated alumina (g)

At time, $t = 0$, the initial rate of fluoride removal is the forward rate alone, therefore:

$$(Q / m)(F_0 - F) = k_1F_1^x, \text{ at } t = 0 \quad (4)$$

A plot of equation (4) in the logarithmic form will yield k_1 and x:

$$\log[(Q / m)(F_0 - F)] = \log k_1 + x \log F_1 \quad (4a)$$

At any given time, F_2 may be calculated by an integration of the breakthrough curve:

$$F_2 = \int_0^t r\,dt \quad (5)$$

or

$$F_2 = (Q / m) \int_0^t (F_0 - F)\,dt \quad (6)$$

k_2 and y can then be determined from the logarithmic form of equation (2):

$$\log(k_1F_1^x - r) = \log k_2 + y \log F_2 \quad (2a)$$

Using Q = 0.2 L/min and a mesh size of 48 to 80, experimental data showed that:

$$r = 0.0322\ F_1^{\,0.854} - 0.14\ F_2^{\,0.844} \quad (7)$$

The selected flow rate was believed to be sufficient to create adequate turbulence to overcome the film diffusion effect while the mesh size chosen seemed to minimize the pore diffusion effect.

Equation (7) can be used to predict the equilibrium condition by letting r = 0, thus giving:

$$F_2 = 0.175\ F_1^{\,1.011}, \text{ at equilibrium} \quad (8)$$

The results of a simple batch experiment showed a good fit of this relationship.

3.2.5.4 Fluoride Removal Isotherms

The adsorption isotherm provides a good indication of the effectiveness and capacity of an adsorbent in removing an impurity. It may be determined from the results of either equilibrium batch tests or column exhaustion tests. The latter would be a better indication of the actual performance. There are two common empirical models of adsorption isotherms:

Langmuir Isotherm: $qe = Q^{\circ}\, b\, Ce / (1 + b\, Ce)$ (9)

Freundlich Isotherm: $qe = K\, Ce^{1/n}$ (10)

where,

qe = solute ion adsorbed per unit mass of activated alumina (mg/g)

Ce = equilibrium solute concentration in solution (mg/L)

Q° = maximum monolayer concentration of solute ion adsorbed on the alumina surface (mg/g)

K, b, n = constants

These isotherms are normally plotted in the linearized form so that the constants (Q°, K, b, n) are conveniently represented by the slope and the intercept. Researchers generally agree (Bishop and Sansoucy 1978; Singh and Clifford 1981; Wu and Nitya 1978) that fluoride removal by activated alumina can be better described by the Langmuir isotherm than the Freundlich isotherm. This suggests that activated alumina behaves like a weak base synthetic resin and that the removal is a single-layer adsorption process. Singh and Clifford (1981) applied the Langmuir multi-component equilibria theory (binary adsorption isotherms) to hydroxide and fluoride ions and found that hydroxide adsorption is much preferred to fluoride adsorption. This finding justifies the acid conditioning and regeneration processes. Some

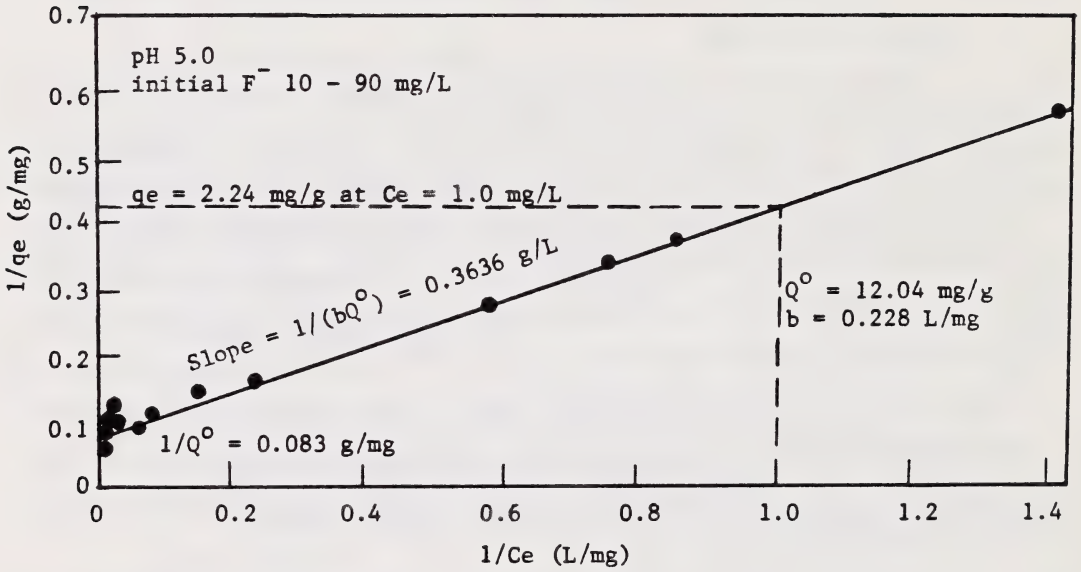
experimentally determined isotherms of activated alumina in removing fluorides are shown in Figures 12 to 14.

The shape of an adsorption isotherm may be affected by the relative affinity of the solute to the solid, the number of available sites or the interaction of adsorbed molecules (Singh and Clifford 1981). In a Freundlich plot (log-log scale) of the equilibrium fluoride adsorption isotherm of activated alumina, Choi and Chen (1979) found an abrupt change in the slope of the isotherm (Figure 14). The differences in the availability and fluoride affinity of different sites may be a contributing factor. The sharp change in slope may mark the saturation of more readily available sites requiring the occupation of the less active sites.

3.2.5.5 Removal Capacity

The useful capacity of activated alumina in removing fluorides can easily be confused by the wide variations reported in the literature. One should be aware of the fact that the fluoride removal capacity of activated alumina is highly dependent on the operating conditions and the method of regeneration. Fluoride removal capacity is particularly sensitive to pH, alkalinity and fluoride concentration of the feed water. Without adequate knowledge of the optimum conditions, early literature generally reported capacities that do not appear to be any more favourable than those reported for bone char. With improved operating practices and careful control of the process environment, based on a better understanding of the factors affecting fluoride removal by activated alumina, actual operating capacities in full-scale plants (Rubel and Woosley 1979) have increased four fold since the first activated alumina defluoridation plant was built in 1952.

Some reported capacities from the literature are presented in Table 5 together with the known conditions. Experimentally determined capacities found in the literature have been based on either continuous column flow or batch reactor studies. Results of a continuous flow study are likely a better indication of actual performance in a plant. The capacities determined from batch studies are the equilibrium capacities of the adsorbent at various equilibrium fluoride concentrations. A plot of this isotherm can determine the total capacity, Q°, of the adsorbent (Figure 12). In continuous flow studies, the capacity determined depends on the arbitrary breakthrough point chosen. The total capacity may also be determined in this case by running the column to exhaustion at various influent fluoride concentrations and plotting the resulting isotherm (Figure 13). By running the column to exhaustion, the exhaustion capacity is



*Equilibrium batch test results

Figure 12. Langmuir isotherm for fluoride adsorption on activated alumina
Experimental results from Wu and Nitya (1979)

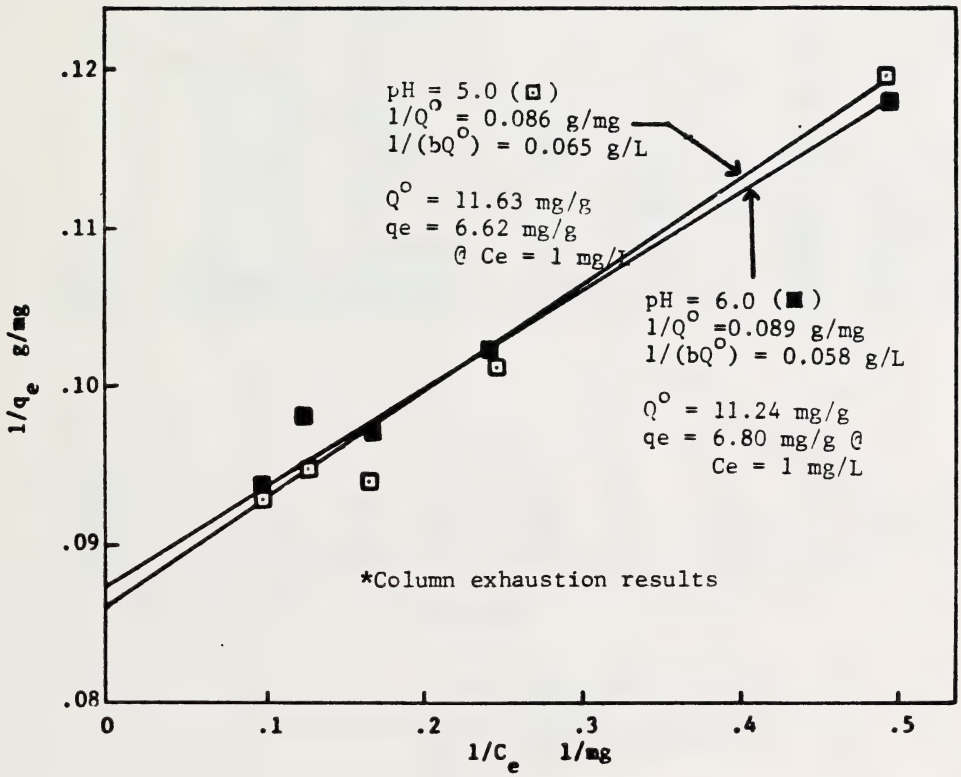


Figure 13. Langmuir isotherms for fluoride adsorption on activated alumina

Experimental results from Singh and Clifford (1981)

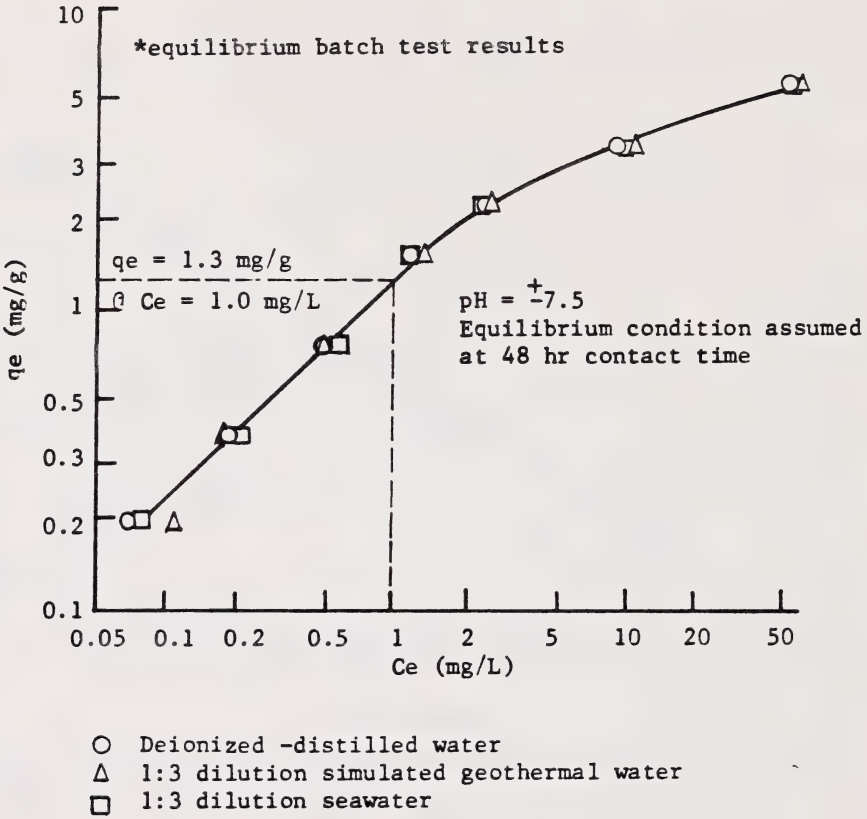


Figure 14. Freundlich isotherm for fluoride adsorption on activated alumina

Experimental results from Choi and Chen (1979)

Table 5. Fluoride removal capacities of activated alumina

REFERENCE	CAPACITY (g/m^3 or *mg/g)	COMMENTS
Pilot/Laboratory scale		
Boruff 1934	675	- calculated by Savinelli and Black (1958) from original column test data; exact basis of calculation unknown - varied test conditions; natural pH
Fink and Lindsay 1936	950	- calculated by Savinelli and Black (1958) from original column test data; exact basis of calculation unknown - varied test conditions; pH 6.5 - 8.5
Swope and Hess 1937	1,155	- calculated by Savinelli and Black (1958) from original column test data; exact basis of calculation unknown - varied test conditions; natural pH
Goltz 1938, cited by Savinelli and Black 1958	1,370	- rated capacity, based on a patented regeneration process
Maier 1953	1,180	- useable column capacity, based on pilot work at Bartlett - initial F^-, 8 mg/L; average effluent F^-, 1 mg/L; pH 7.8
Savinelli and Black 1958	7,800	- exhaustion capacity of column - NaF supplemented tap water; initial F^-, 10 mg/L; pH 5.6; flow rate, 55 L/min/m^2; alum regeneration
Sollo *et al.* 1978	5.6* (4,500)	- column breakthrough capacity, based on 1 mg/L equivalent F^- in total treated water - synthetic water; initial F^-, 4 mg/L; pH 7; flow rate, 60 - 80 L/min/m^2 (0.6 - 0.8 L/min/kg)
Bishop and Sansoucy 1978	3,500	- exhaustion capacity of fluidized column - initial F^-, 10 mg/L
	2,500	- breakthrough capacity of fluidized column, based on 0.5 mg/L effluent F^- - initial F^-, 10 mg/L
	1,700	- exhaustion capacity of fluidized column - initial F^-, 4 mg/L
	1,000	- breakthrough capacity of fluidized column, based on 0.5 mg/L effluent F^- - initial F^-, 4 mg/L

Table 5. Fluoride removal capacities of activated alumina (continued)

REFERENCE	CAPACITY (g/m^3 or *mg/g)	COMMENTS
Wu and Nitya 1979	12.04* (9,600)	- batch test maximum equilibrium capacity - pure F^- solution; initial F^-, 10 - 90 mg/L; pH 5.0
Hung 1981	1,900	- column breakthrough capacity, based on 1 mg/L effluent F^- - natural water; natural pH; initial F^-, 9.5 mg/L; 80 to 200 mesh; upflow 160 L/min/m^2 (1.3 L/min/kg)
Singh and Clifford 1981	10.2* (8,000)	- average exhaustion capacity of column - pure F^- solution; initial F^-, 2 - 10 mg/L; pH 5 - 6; flow rate, 5 - 42 L/min/m^2 (0.5 - 4.0 L/min/kg)
Full scale		
Maier 1953,1960		
Bartlett, Texas	750 - 935	- initial F^-, 8 mg/L; average effluent F^-, 1 mg/L; pH 7.8
	1,600	- pH lowered to 7.2
	915	- new water source; initial F^-, 3 mg/L
Rubel and Woosley 1979		
Desert Center, California	>4,600	- initial F^-, 8 mg/L; average effluent F^-, 1 mg/L; pH 5 - 6
Vail, Arizona	>4,600	- initial F^-, 5 mg/L; average effluent F^-, 1 mg/L; pH 5 - 6
Gila Bend, Arizona	>4,600	- initial F^-, 5 mg/L; pH 5 - 6

equivalent to the equilibrium capacity in batch tests (qe), while the influent fluoride concentration is equivalent to the equilibrium concentration (Ce). Bench-scale capacities do not necessarily reflect the useful capacity in an actual plant where the operating capacity is based on reducing fluorides in the treated water to an average concentration equivalent to the acceptable or desirable level.

3.2.5.6 Influent Fluoride Concentration

The capacity of activated alumina for removing fluorides increases with the fluoride concentration of the influent. Increased concentrations of fluoride, which increase diffusivity and activity of the fluoride ion, are believed to enable the use of the less accessible (e.g. interior pore surface) or energetically less active sites (Choi and Chen 1979). When the influent fluoride concentration at the Bartlett plant was lowered from 8 mg/L to 3 mg/L by switching to a new water source, the capacity was reduced from 1,600 g/m^3 to 915 g/m^3. Despite the lower observed capacity, the cycle time between regenerations was longer for the lower concentration (Maier 1960). Bishop and Sansoucy (1978), and Savinelli and Black (1958), found a linear relationship between removal capacity and influent fluoride concentration. However, Singh and Clifford (1981) found that the rate of capacity increase was higher at lower initial fluoride concentrations (Figure 15).

Despite increasing capacity, higher fluoride feed concentrations generally result in shorter runs (Hung 1981; Singh and Clifford 1981). The practical upper limit of fluoride concentration for water to be effectively treated by activated alumina is about 10 mg/L (Parker and Fong 1975).

3.2.5.7 pH

As stated previously, the pH of the water affects the surface charge of activated alumina and the kind of ions adsorbed on the surface. In fact, the activated alumina defluoridation process is very pH sensitive. The optimum range is rather narrow but the sharp decline in removal efficiency outside the optimum range indicates the possibility of relatively easy regeneration by either acid or alkali (Choi and Chen 1979). During the early development of the activated alumina process, Fink and Lindsay (1936) suspected the dependence process efficiency and fluoride removal capacity upon pH, and suggested the possibility of acidifying the feed water. The optimum pH is now known to be in the 5 to 6 range. Not only are the

removal efficiency and capacity highest in this range, the adsorption rate is also at the maximum (Wu and Nitya 1979), and interference by competing ions is minimal (Rubel and Woosley 1979). The treatment process therefore requires acidification of the feed water and/or alumina. However, the effluent pH must be raised before the treated water can be distributed.

Activated alumina preferentially adsorbs F^-, CO_3^{2-} and HCO_3^- at pH 5 to 10 (Rigdon 1980). Within this range, the adsorption of F^- increases as the pH decreases and the competing alkalinity is neutralized:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

The hydroxyl ion is definitely the most important competitor to the fluoride ion as the former tops the anion selectivity sequence. Under acidic conditions, the alumina will release the hydroxyl group to neutralize acidity, making more sites available for F^- (Bishop and Sansoucy 1978). At pH 7, OH^- begins to compete with F^- for sites. Above pH 8, the predominant OH^- ion is preferred. A steep decline in fluoride removal capacity is therefore evident at pH 6 to 7.5 (Singh and Clifford 1981) as shown in Figure 15. According to Choi and Chen (1979), the principal anion adsorption sites will gradually disappear above pH 8.5, forming an increasingly negatively charged surface.

Below pH 5, activated alumina dissolves to form aluminum complexes with the fluoride ion (AlF^{2+}, AlF_2^+, AlF_3, AlF_4^-, etc.) until all the adsorbent dissolves to form ligand compounds (Singh and Clifford 1981). At the same time, the surface of the alumina becomes more positively charged as the pH decreases. The electrical repulsion between the positively charged complexes and the positively charged surface results in a sharp decline in fluoride removal (Choi and Chen 1979).

3.2.5.8 Competing Ions

The importance of pH control in the activated alumina process is strongly associated with its role in neutralizing alkalinity. Alkalinity-causing ions can significantly hinder fluoride removal as a result of competition. Bishop and Sansoucy (1978) found a reduction in alkalinity during fluoride removal in a batch reactor. The data signify that, for a given initial fluoride concentration, a fixed amount of alkalinity will be removed regardless of the initial alkalinity. Accordingly, waters of low alkalinity might have all their buffer capacity removed by the process. Savinelli and Black (1958) traced the drop and rise of alkalinity during the exhaustion

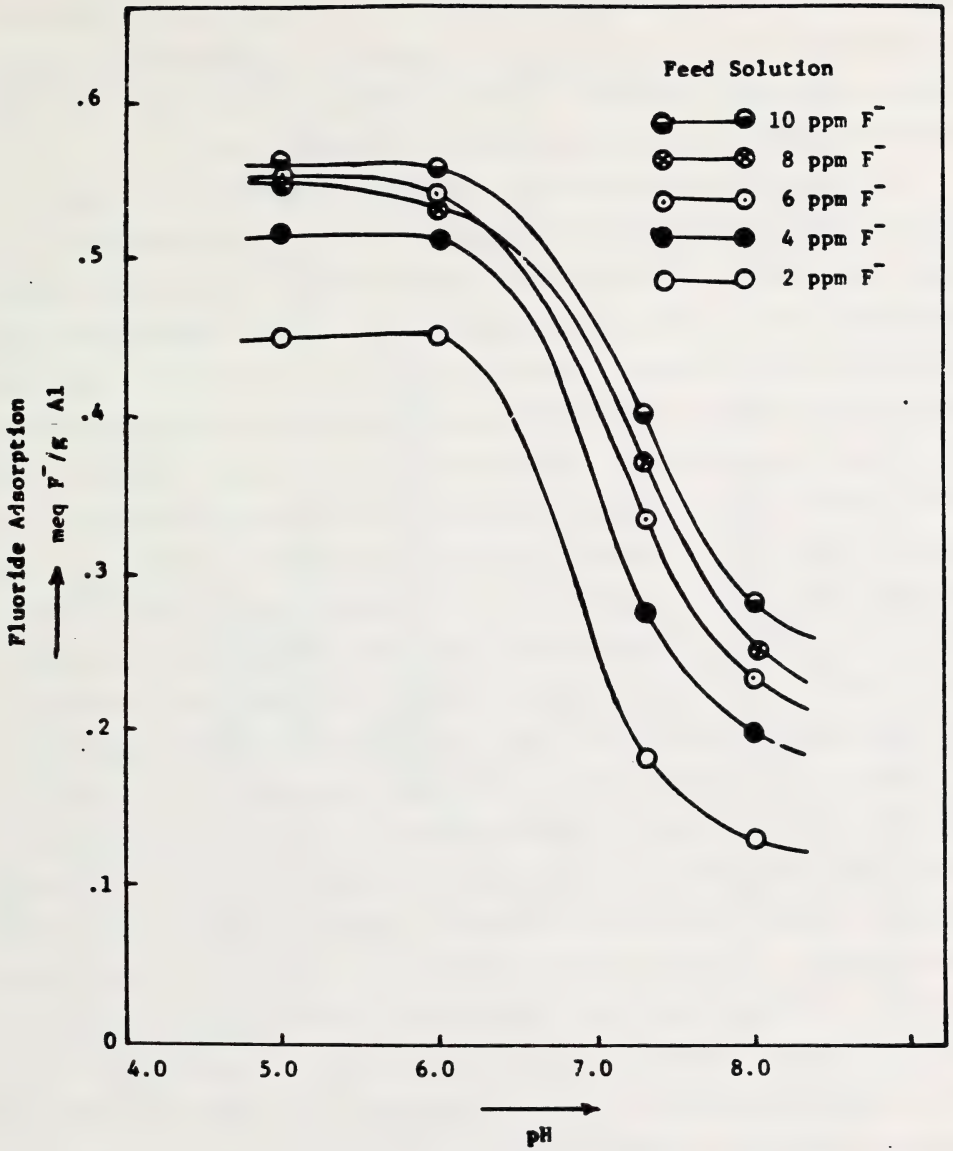


Figure 15. Effects of pH and initial F^- concentration on fluoride capacity of activated alumina (Singh and Clifford 1981)

phase of a column study. Typically, all the alkalinity was removed during the first half of the run but returned steadily later in the run. By comparison, the fluoride removal efficiency continued to improve to a maximum at 75 per cent of the run. The pH began to rise as the alkalinity and fluoride concentrations increased in the later stages of the run.

On the basis of the anion selectivity sequence of activated alumina, the fluoride ion is highly preferred and most common anions cannot easily compete with it for sites. However, if present in large quantities, the possible effects of the less preferred anions on fluoride removal are of interest. Savinelli and Black (1958) found little effect for either sulphate or chloride ion on the fluoride removal capacity of activated alumina up to a concentration of 1,000 mg/L. Sulphate concentrations up to 2,000 mg/L did not affect the fluoride removal efficiency in the batch experiment conducted by Choi and Chen (1979). In the same study, the salinity test also indicated that the removal efficiency was not affected by the increase in chloride salts. Singh and Clifford (1981) found measurable competition by the sulphate ion on fluoride removal as depicted in Figure 16. The curves show that as the sulphate concentration went up, sulphate adsorption increased and the fluoride removal capacity decreased. Based on this observation, a capacity reduction of as high as 26 % would be possible for high fluoride waters containing 250 mg/L sulphate. On the other hand, increasing chloride concentration showed no negative effect on the fluoride removal capacity, indicating that chloride competition may be far too poor to pose any threat to fluoride removal. Further observations on total anion adsorption indicated that the same milliequivalence of total anions was adsorbed for a given total anionic concentration (meq/L) regardless of the anionic composition. Moreover, total anionic adsorption appeared to increase with the total concentration of anions. This finding suggests that when two ionic species with a large separation factor (preferential adsorption of one over the other) are present, adsorption of the more preferred species may possibly improve in the presence of higher concentrations of the less preferred species as long as adsorption of the latter is relatively independent of concentration (Singh and Clifford 1981).

Groundwaters are typically high in total dissolved solids with SO_4^{2-}, Cl^-, HCO_3^-, CO_3^{2-} and NO_3^- as common anions. Hung (1981), and Singh and Clifford (1981), have shown evidence of reductions in fluoride removal efficiency and capacity with increase in total dissolved solids. Singh and Clifford claimed that the sulphate ion was mainly responsible.

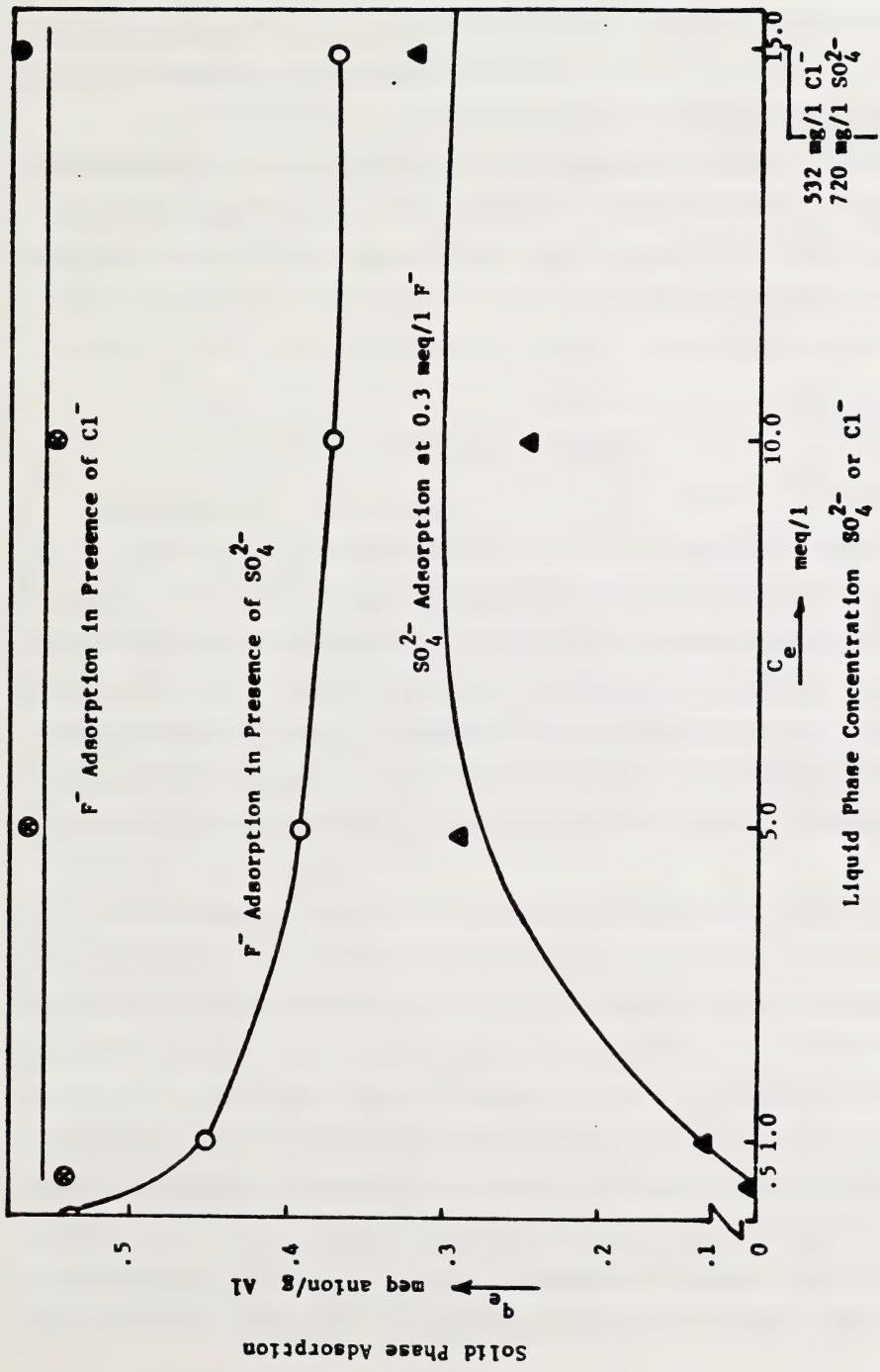


Figure 16. Effects of SO_4^{2-} and Cl^- on activated alumina defluoridation

(Singh and Clifford 1981)

There have been reports of cation removal during fluoride removal. Reduction of total hardness has been observed during fluoride removal (Maier 1953; Savinelli and Black 1958; Swope and Hess 1937). However, it is not clear whether this can be regarded as an added benefit or an indication of interference. It is likely that the hardness ions occupy a different kind of sites from those reserved for anions.

Clifford *et al.* (1978) reported activated alumina as a suitable adsorbent for silica. Choi and Chen (1979) found a reduction in fluoride removal with increased concentration of dissolved silica. This may be a result of competition for available sites and deactivation effects on some sites caused by the adsorption of silica. Arsenic removal and interference will be discussed in a later section.

3.2.5.9 Flow rate

The effects of flow rate during a treatment run on fluoride removal by activated alumina columns are related to the fluoride adsorption rate of activated alumina. The adsorption process is considered fairly slow. The rate slows down as sites are filled and it takes a long time to reach equilibrium after breakthrough (Singh and Clifford 1981). There has been evidence that activated alumina will continue to remove additional contaminants when the system flow is temporarily shut off to allow batch contact (Bellack 1971). A slower flow rate will apparently provide a longer contact time and thus better opportunity for fluoride removal. Singh and Clifford (1981) have shown that as the flow rate goes up, the total throughput at exhaustion increases. The throughput is referred to meq F^- passed through the bed per meq F^- capacity.

Boruff (1934) found that when the flow rate was lowered from 0.67 L/min/kg (535 L/min/m^3) to 0.17 L/min/kg (134 L/min/m^3) during a treatment run, an additional removal of fluorides was immediately achieved. A still lower rate, however, may not be desirable or even practical. Swope and Hess (1937) compared the performance of two flow rates, 0.75 L/min (0.17 L/min/kg, comparable to the lower rate used in Boruff's study) and 0.32 L/min (0.07 L/min/kg), and surprisingly found a higher fluoride capacity associated with the higher rate. The difficulty in removing fluorides at too low a flow rate may be explained by Wu's and Itemakin's (1979) theory of film diffusion effect. These researchers varied the volumetric flow rate, Q (L/min), but kept the bed loading constant at 30 L/min/kg by changing the amount of activated alumina. This high loading rate was used because it was an upflow column. The initial

adsorption rates observed indicated that film diffusion was operative below 0.12 L/min, and that a Q of 0.19 L/min would be required to eliminate this effect. It is possible that within the practical ranges of flow and bed size, the film diffusion effect will become predominant at a low flow/alumina loading.

When the flow rates in Boruff's study (1934) are converted to surface loadings, the high and low rates become 208 L/min/m^2 and 52 L/min/m^2, respectively. Within this range, a lower rate increased the removal efficiency. Savinelli and Black (1958) found that fluoride capacity of their 25 mm columns did not decrease until the flow rate was raised above 2 L/hr which corresponds to a surface loading of 66 L/min/m^2. This again indicates that if Boruff had lowered his rate further, improvement may not have been signifcant. Practical considerations often dictate a lower limit on flow rates. Bellack (1971) established an optimum rate of 100 to 120 L/min/m^2 based on observations of arsenic removal.

3.2.5.10 Bed Size

The amount of activated alumina required in treatment is determined by the fluoride capacity, the quantity of fluoride to be removed, and the desirable cycle length. The capacity, as mentioned, is a function of many variables. For the design of an actual plant, pilot work should be conducted to truly assess the serviceable capacity for the particular water concerned. In regards to cycle length, it is desirable to keep the regeneration periods reasonably long in order to minimize regeneration cost and overall down-time. A cycle longer than two weeks is not recommended because cycle variations in fluoride concentration may lead to possible physiological effects (Dangel 1977).

The required bed surface area is governed by the flow rate. Once the former is established, the bed depth may be determined. Sometimes, a compromise must be made between an efficient surface loading rate and a practical area-to-depth ratio. The bed depth should be at least 1 m in order to avoid channeling and bypassing (Bellack 1971).

The results of Hung's (1981) work showed that the efficiency of activated alumina, expressed as F^- removal/amount of alumina, decreased with increased alumina. This is in general agreement with earlier work by Bishop and Sansoucy (1978), which revealed that fluoride removal increased with bed depth but only up to a maximum level. An excess of media will result in alkalinity occupying the sites not taken by fluoride. The column capacity for fluoride will be correspondingly reduced and the already waning buffer capacity will be lowered

further. It may be desirable to start at a shallow depth and increase it as the column becomes exhausted by adding alumina to the influent.

3.2.5.11 Particle Size

Activated alumina of smaller particle sizes naturally has larger surface area per volume and therefore higher capacity for fluoride removal (Bishop and Sansoucy 1978; Hung 1981). In addition, decreasing the particle size will reduce pore diffusion effects and increase the initial rate of fluoride removal (Wu and Itemakin 1978). For a fluidized bed, large particle sizes would require unfavourably high fluidization velocities at which removal would become difficult. Too small a size would be difficult to contain in the fluidized column. Bishop and Sansoucy (1978) established an optimum mesh size of 35 to 50 for fluidized beds. Static columns in full-scale plants typically use 28 to 48 mesh Alcoa F-1 grade particles.

3.2.5.12 Modes of Flow Application

An activated alumina defluoridation unit may operate under gravity or pressure although experimental works have generally used gravity-flow systems. The progressive increase in back pressure during treatment, in either case, limits the flow rate in the gravity system and increases the pumping requirements in the pressurized system (Bellack 1971).

A pressurized system may operate in downflow or upflow mode, or the bed may be fluidized by the upflow. When the bed is fluidized (Bishop and Sansoucy 1978), more surface area will become available and removal capacity will increase. A much higher loading rate can be tolerated in a fluidized than in a static bed for the same removal. These factors permit a smaller unit for the fluidized system. Moreover, the problem of clogging is lessened when the bed is fluidized. Bishop and Sansoucy used a fluidization velocity of 490 $L/min/m^2$ to achieve 100 % bed expansion for the 35 to 50 mesh alumina.

3.2.5.13 Regeneration

The possible mechanism involved in regenerating activated alumina for fluoride removal has been described in Section 3.2.5.2. The regeneration follows the generalized procedure outlined in Section 3.2.1. More detailed operational guidelines will be presented in a later section.

The renewed fluoride capacity of activated alumina after regeneration depends on the efficiency of the regeneration method. Swope and Hess (1937) claimed that more than 100 %

efficiency could be achieved based on observations that the capacity actually improved after regeneration. The regenerants used were 5 % NaOH and 0.35 % HCl. The tests, however, did not carry far enough to prove this continuous trend. It is possible that the original activated alumina supplied may have contained impurities which may have been gradually dislodged through regeneration. The data of Rubel and Williams (1980) pilot works show that the first regeneration was always less than 100 % efficient. However, as the treatment proceeded, fluoride recovered in regeneration equalled fluoride removed in the previous run. The regeneration used either 1 % NaOH or 4 % NaOH (for additonal arsenic recovery), and dilute H_2SO_4. Sulphuric acid was considered more economical than hydrochloric acid for bed neutralization.

The efficiency of regeneration apparently depends on the total amount of caustic used. A larger volume of lower strength solution will be required to achieve the same level of efficiency as a lower volume of higher strength solution (Bishop and Sansoucy 1978). Full-scale plants typically use a weak 1 % NaOH solution in order to minimize bed dissolution. A sufficient volume of this solution must be applied to ensure full regeneration of the bed. At the Bartlett plant (Marier 1953), about 20,000 L was used, corresponding to 1,400 L/m^3 bed volume. A caustic alkalinity began to emerge in the waste effluent near the end of this passage.

Although Swope and Hesse (1937) showed that the spent caustic solution could be reused, it is being discarded in operating plants due to excessive contamination. The Bartlett plant did try to conserve part of the caustic by reusing a portion of the rinse water. Figure 17 shows that the caustic return may start when most of the fluoride has been removed from the bed, and the alkalinity is just starting to be rinsed out in large quantities. The idea is to collect as much caustic as possible while keeping the fluoride away. The plot also indicates that the economical quantity of rinse water to be used before acid neutralization can be determined from the asymptotic point of the alkalinity curve.

Savinelli and Black (1958) reported on the use of a dilute solution of aluminum sulphate alone for regeneration. This was expected to achieve fluoride removal from the exhausted bed by ion exchange with aluminum hydroxide flocs. Alum regeneration of activated alumina has been tried in a full-scale plant but with disappointing results (Harmon and Kalichman 1965). The difficulties included low pH of the treated water, unpredictable capacity, and aluminum release in the treated water.

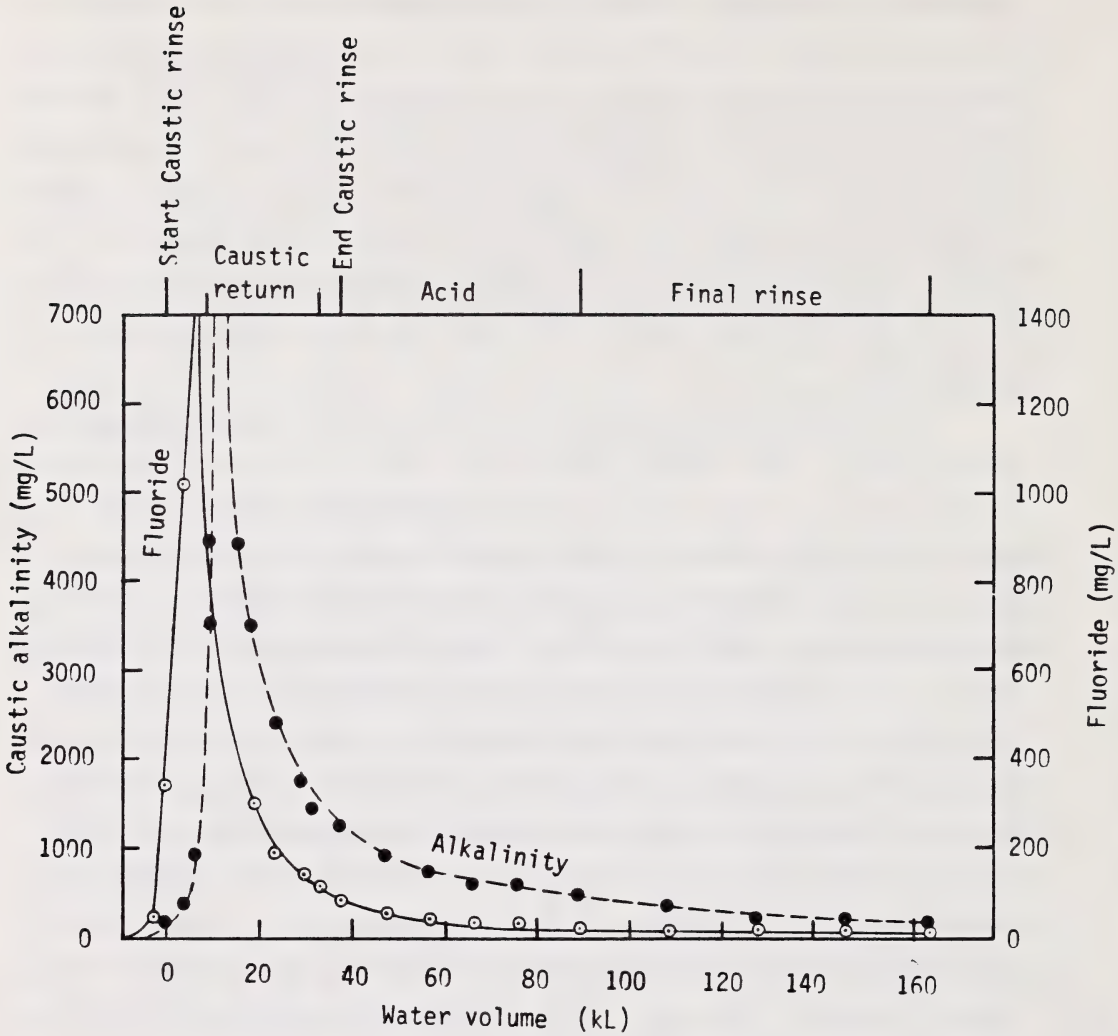


Figure 17. Concentration curves for caustic alkalinity and fluoride during caustic rinse and neutralization, Bartlett Plant, Texas (Maier 1953)

3.2.5.14 Combined Treatment for Fluoride and Arsenic Removal

Like bone char, activated alumina exhibits considerable capacity for arsenic adsorption but the accumulated arsenic is not easily removed from the media by regeneration. Bellack (1971) examined the feasibility of using the activated alumina defluoridation process to accommodate arsenic removal during the normal fluoride removal cycle. Initially arsenic recovery during regeneration was only 12.5% when using 1 % NaOH. Although complete recovery could be achieved using 10 % NaOH, it was not considered practical for fear of bed dissolution. Fortunately, even with 1 % NaOH, it later appeared that an equilibrium point of arsenic accumulation (1 mg/g alumina) was eventually reached when arsenic removal equalled arsenic recovery. At this equilibrium point, the alumina still showed adequate capacity for arsenic removal when the influent arsenic concentration was 0.06 mg/L. The fluoride capacity remained unchanged at 2.13 mg/g, removing 3.8 mg/L fluoride.

A more recent pilot plant study by Rubel and Williams (1980) showed that the arsenic retained in the bed after regeneration interfered with fluoride removal and lowered the fluoride capacity in subsequent runs. A higher volume of caustic regenerant improved fluoride recovery but not the arsenic. A 4 % NaOH solution rather than 1 % proved to be more efficient in regenerating the bed for both arsenic and fluoride. A two-stage treatment process was tested and appeared to provide better utilization of the bed capacity for both arsenic and fluoride removal. The first stage was designed for arsenic removal based on the anticipation that activated alumina would continue to preferentially adsorb arsenic after fluoride saturation. The second stage was primarily for fluoride removal in the absence of arsenic. A 4 % NaOH solution for the first stage and 1 % for the second stage were used in regeneration. More alumina was solubilized by 4 % NaOH than by 1 % NaOH but a decreasing trend with each regeneration was evident. An annual bed replacement of 10 % was estimated for this two-stage system, as compared to 3 % for the normal process using 1 % NaOH.

The arsenic and fluoride concentrations in the raw water were 0.14 mg/L and 3 mg/L, respectively, in the above study. Figure 18 shows the concentration curves of the two-column system during a typical treatment run which terminated at second stage fluoride breakthrough. The fluoride removal capacity of the first column was about 4,300 g/m^3, obviously corresponding to fluoride saturation. The second column removed about 3,300 g/m^3 fluoride based on a breakthrough at either 2.4 mg/L in the effluent or an equivalent of 1.1 mg/L in the

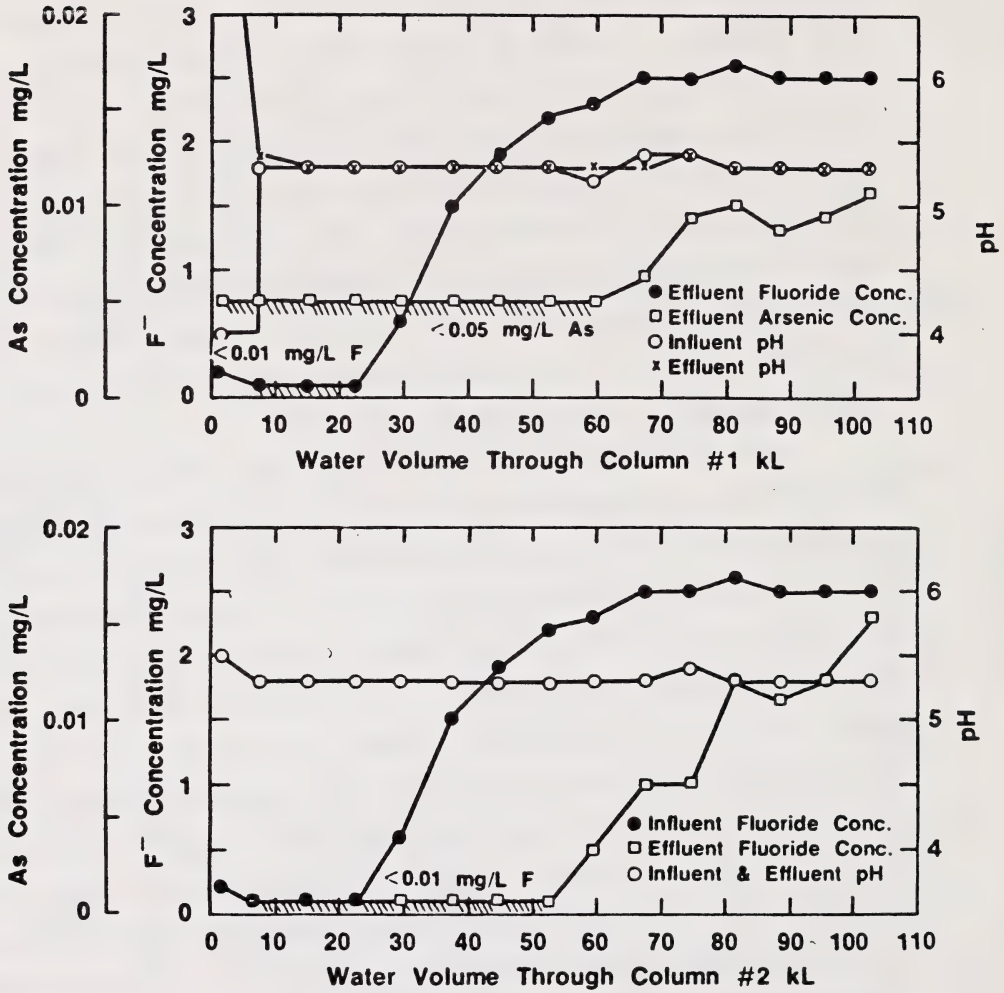


Figure 18. Concentration curves of a 2-stage activated alumina system during exhaustion phase

(Rubel and Williams 1980)

average concentration.

2.2.5.15 Recommended Operating Practices

Rubel and Woosley (1979) have recommended some operational procedures for the activated alumina defluoridation process based on the experience of three modern plants. The interesting features are the two-step caustic regeneration and that a portion of the treatment run is incorporated into the neutralization step. An outline of the procedures is summarized as follows:

Initial start-up

1. The column is half-filled with water which then dissipates the heat of wetting when the alumina is poured in, thereby preventing cementing of the alumina. The water also separates fines from the granular material, protects the underdrain from impact and initiates stratification of the bed material.
2. The bed is backwashed for an extended period to flush out all the fines.

Treatment

1. The influent pH is adjusted to between 5 and 6 by H_2SO_4 injection at a rate that depends on the raw water alkalinity.
2. A 5 min residence time of water in the bed is required for maximum removal efficiency.
3. Wall effects or channeling must be avoided.
4. When the residual fluoride drops to the acceptable limit (not necessarily the desirable level), the treated water can go to storage or distribution.
5. The effluent pH is lowered or raised to near the neutral level by an appropriate neutralizing agent or by blending.
6. The treatment terminates when the average fluoride level in the total finished water reaches the desirable or prescribed level.

Regeneration

1. The bed is backwashed, normally for less than 10 minutes, by an upward flow of 350 L/min/m^2 to achieve about 50 % expansion.
2. A 1 % NaOH solution is prepared with raw water by in-line dilution of 50 % NaOH which

has been kept above 20 °C to prevent freezing.

3. An upflow regeneration with this solution at 100 L/min/m² takes place immediately after the backwash while the bed is still expanding. The process takes about 35 min for a standard 1.5 m bed depth.
4. An upflow rinse follows at 200 L/min/m², taking about 30 min for the standard bed depth.
5. The flow rates and times must be adjusted in accordance to the bed depth.
6. After the unit is drained down to the top of bed, the 1 % NaOH solution is re-applied, downward this time, with the same rate and time as before.
7. The unit is again drained and causticity of the bed is removed by feeding at the normal treatment flow rate raw water that has been acidified to a pH of 2.5.
8. As the pH of the effluent drops and the treatment capacity of the bed starts to function, the pH of the influent is raised stepwise from the initial 2.5 to the final level of 5 to 6 where normal treatment process resumes (Figure 19).
9. The last portions of the effluent during neutralization with satisfactory fluoride levels are directed to storage or distribution as finished water after pH lowering.

Water with a uniform concentration of residual fluoride can be delivered when a large reservoir is available for blending. Alternatively, two units can operate at staggered cycles and produce, at any time, both high- and low-fluoride waters that can be mixed in the watermain. Nevertheless, short-term variations of fluoride level are not harmful and therefore blending is not essential if the cycle length is reasonable. Mixing product waters from two units operating at different stages in their cycle is sensible because their respective pH values may neutralize one another but the interaction will vary with time.

The total volume of the regeneration wastewaters is about 4 % of the total plant throughput based on the recommended procedures. The backwash wastewater may be discharged to the sewer. High-fluoride waste must be safely disposed of. One method is to concentrate the waste in lined evaporation ponds. The concentrated waste is transferred to an acceptable disposal site, or the fluoride is reclaimed.

The operation requires extraordinary care in handling and control of acid and base, and a great deal of accurate water analyses. The chemical storage and handling equipment must be constructed of materials resistant to concentrated acids or bases. Other materials in the

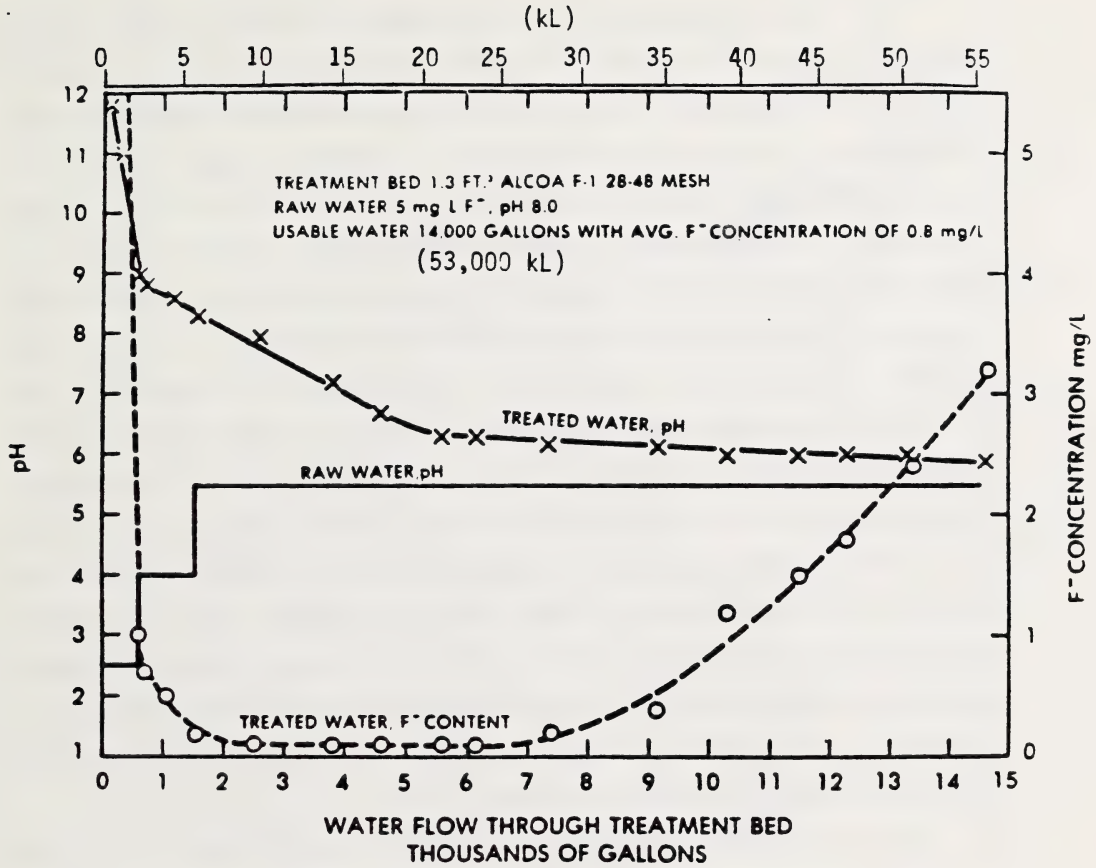

(kL)
0 5 10 15 20 25 30 35 40 45 50 55
TREATMENT BED 1.3 FT.³ ALCOA F-1 28-48 MESH
RAW WATER 5 mg L F⁻, pH 8.0
USABLE WATER 14,000 GALLONS WITH AVG. F⁻ CONCENTRATION OF 0.8 mg/L
(53,000 kL)
TREATED WATER, pH
RAW WATER pH
TREATED WATER, F⁻ CONTENT
pH
F⁻ CONCENTRATION mg/L
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WATER FLOW THROUGH TREATMENT BED
THOUSANDS OF GALLONS

Figure 19. Concentration curves during typical pilot plant run

Gila Bend, Arizona

(Rubel and Woosley 1979)

treatment system must also withstand a wide range of pH conditions from 2 to 13. The operator must be specially trained for the process, with full awareness of the safe chemical handling requirements; and skills in fluoride analysis and in record keeping.

3.2.5.16 Costs

Many cost factors pertaining to bone char systems also apply to activated alumina systems. The construction costs should not differ significantly between these two types of systems; both should generally reflect the cost of an ion exchange system. But the activated alumina material, at about $\$500/m^3$ (1978 dollars), is considerably cheaper than bone char (Sorg 1978). Besides, bed replacement frequency for activated alumina is expected to be lower. A great deal of pH adjustment, in addition to regeneration, is included in the chemical expenditures of activated alumina treatment. Depending on the plant size and location, bulk purchase of 50 % liquid caustic and 66° Baume sulphuric acid (93.19 % H_2SO_4) is generally most economical. Like the bone char system, labour is primarily required in the regeneration phase. Some labour is also involved in sampling, analysis and maintenance. A part-time plant operator would probably suffice. Automation of the regeneration sequence and installation of continuous pH monitoring and control devices will reduce labour but increase the capital cost.

Activated alumina at favourable conditions has higher fluoride capacity than bone char. Therefore, for the same bed size and influent fluoride concentration, the activated alumina system will have a lower operating cost than the bone char system as a result of less frequent regeneration. However, the cycle length for both systems is normally restricted to about two weeks. For the same productivity, the size of equipment for the activated alumina process can be reduced as compared to the bone char process.

Rubel and Woosley (1979) reported a typical cost range of \$0.02 to 0.05/kL for operation of the activated alumina process, and that a plant at Gila Bend, Arizona (4.8 ML/d capacity) had been constructed for less than \$200,000 during 1977 to 1978. Figures 20 and 21 are construction and operation cost curves developed by Gumerman *et al.* (1979, cited by Sorg 1980) for activated alumina defluoridation plants. The operation cost curve does not include chemical or disposal costs. The chemical cost may be taken as \$0.01 to 0.02/kL, typical to those reported by Rubel and Woosley (1979) for existing plants. These curves appear to agree roughly with other reported plant data or estimates (Rigdon 1980; Rubel and Woosley 1979; Rubel and Williams 1980). O'Brien (1983) has provided some recent estimates of total

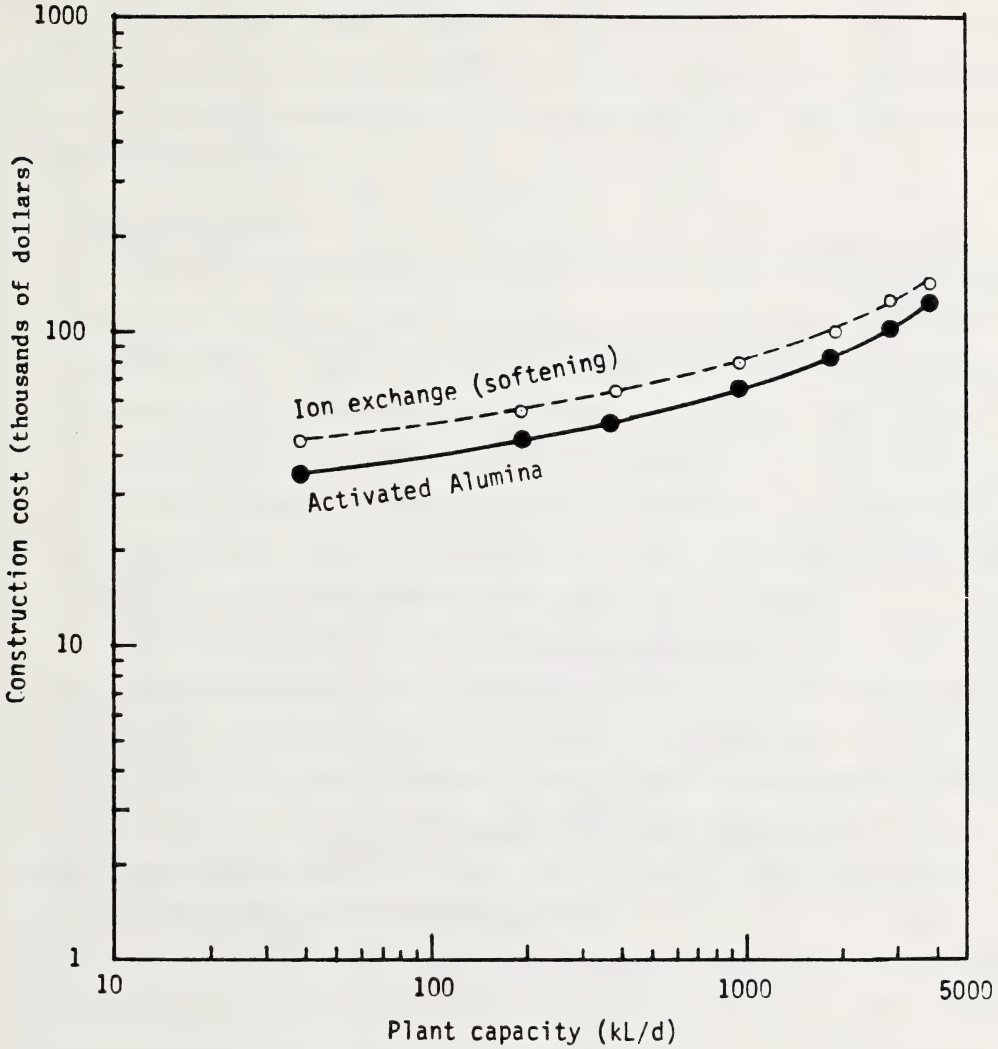


Figure 20. Construction cost for activated alumina defluoridation plants

(source: Sorg 1980, after Gumerman *et al.* 1979)

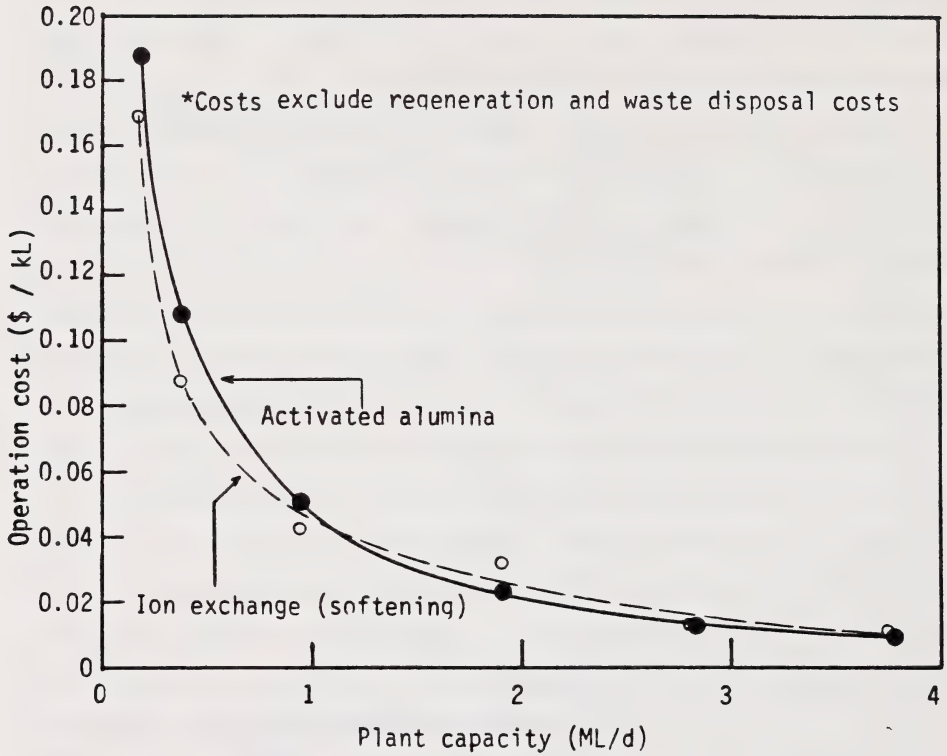


Figure 21. Operation cost for activated alumina defluoridation

(source: Sorg 1980, after Gumerman *et al.* 1979)

treatment costs for various processes, based upon capital amortized on a 20-year term at 12 %. A plot of these estimates (Figure 30) is given in the concluding section of this report, showing how the activated alumina process compares with the others. For a 1.0 ML/d activated alumina plant, the treatment cost was about $0.16/kL according to the plot. Waste disposal was not included in these estimates.

3.2.5.17 Case Studies

As of 1979, there were three large-scale activated alumina defluoridation plants operating in the United States (Rubel and Woosley 1979); at Desert Center, California; Vail, Arizona; and Gila Bend, Arizona. The rated plant capacites were 2.7 to 5.7 ML/d. These plants had been successfully lowering the fluoride concentrations in the water supplies from 5 to 8 mg/L to below 1 mg/L. All these plants reported bed capacities for fluoride exceeding 4,600 g/m^3. Operating in an optimal process environment, these plants are considered models for modern plant operation. The operating procedures have been outlined in a previous section (3.2.5.15). The operating costs, excluding amortization, were $0.03 to 0.04/kL.

The pioneer and longest-operating of all municipal activated alumina defluoridation plants was the Bartlett plant in Texas. Its performance during its years of operation from 1952 to 1977 has been well documented (Maier 1953, 1960; Horowitz and Heifetz 1972). This has provided valuable information for continuous refinement of the activated alumina process. The equipment was similar to that at the Britton bone char plant except that the filter tank was gravity-type instead of pressure-type. Flow control through the filter was automated. No manual operation was involved in the handling of acid.

The life-long plant data at Bartlett are summarized in Table 6 along with the recorded improvements in the operating procedures. The data clearly show that when the raw water pH was lowered by only 0.6 of a unit, the fluoride capacity of the bed improved drastically. This pH adjustment was also reported to reduce the amount of acid required during regeneration. The data also show that by changing to a lower-fluoride water supply, the fluoride removal capacity decreased but the treatment cycle lengthened. There had been a few changes in the regeneration procedures. The combination of backwash and caustic treatment in one step with countercurrent regeneration conserved the treated water formerly used for backwash. Initial attempts to conserve caustic by reusing spent caustic for caustic solution preparation proved to be impractical because of excessive contamination by other ions. In-line dilution of 50 % liquid

Table 6. **Plant data at Bartlett, Texas**
(Maier 1953, 1960; Horowitz and Heifetz 1972)

	1952	BY 1960	1960 - 1972
Plant capacity	1,500 L/min	1,500 L/min	1,500 L/min
Influent fluoride	8 mg/L	8 mg/L	3 mg/L (new water source)
Effluent fluoride	1 mg/L	1 mg/L	0.85 - 1.0 mg/L
Media	14 m^3 - 28 to 48 mesh	14 m^3 - 28 to 48 mesh	14 m^3 - 28 to 48 mesh
Influent pH	7.8 (natural)	7.2 (adjusted)	7.2 (adjusted)
Cycle length	1.5 - 1.9 ML	3.2 ML	5.7 ML
Bed capacity	750 - 950 g/m^3	1,600 g/m^3	900 g/m^3
Backwash	- 30% expansion at 230 L/min/m^2 for 15 min, requiring 30,000 L treated water	- combined with caustic treatment	- presumably unchanged from 1960
Caustic treatment	- 23,000 L - 1% NaOH at 890 L/min, prepared from spent rinse water and flake caustic	- 19,000 L - 1% NaOH at 890 L/min, prepared from spent rinse water and flake caustic - countercurrent flow for backwash incorporation	- liquid caustic (50%), replacing flake caustic, directly pumped into raw water line
Caustic rinse	- raw water - first 9,500 L discarded - 23,000 L returned to caustic solutin tank - 5,700 - 9,500 L second rinse	- 106,000 L raw water, a portion being returned to fill caustic solution tank	- no return portions
Neutralization	- 50,000 L - 0.05N H_2SO_4 at 830 L/min, prepared from raw water and concentrated acid	- 151,000 L raw water at reduced pH (7.2), bringing effluent alkalinity to that of raw water, and fluoride level to 1 mg/L	- presumably unchanged from 1960
Final rinse	- 76,000 L raw water	- eliminated	- presumably unchanged from 1960
Total regeneration water	about 208,000 L (30,000 L treated water)	about 259,000 L	unknown
Capital cost	$15,000 including media	n/a	n/a
Chemical cost	$14.00/ML	$10.60/ML	$6.60/ML (1960)

caustic was later found more economical. The chemical costs show a continuous decline as the operation improved. The final development of this plant was indeed the forerunner of modern plants.

3.2.5.18 Advantages

1. Activated alumina has a high preference for the fluoride ion and is therefore ideal for specific fluoride removal when the fluoride is present among other less preferred ions.
2. Very high fluoride removal capacity is sustainable for activated alumina when the most favourable environment is maintained.
3. The activated alumina process is effective in reducing fluoride to very low levels.
4. The low water and mechanical wear of activated alumina (Choi and Chen 1979) results in little bed loss providing the regeneration solutions are kept at low strength.
5. Virgin activated alumina is low in leachable impurites (Choi and Chen 1979).
6. Activated alumina is more available and versatile than bone char (O'Brien 1983).
7. Efficient regeneration of the alumina is possible outside the optimum pH range for treatment.
8. The treatment bed does not promote microbial growth; bacterial counts are actually reduced (Fink and Lindsay 1936).
9. The activated alumina process can be used for simultaneous reduction of both arsenic and fluoride.
10. The system can be operated on demand.
11. There have been many years of actual plant experience with the activated alumina defluoridation process.

3.2.5.19 Disadvantages

1. The process requires considerable attention to the optimization of operating conditions, particularly in pH control, or it will become inferior to bone adsorption.
2. The high skills required in operating the process, especially when regeneration is involved, make home application not feasible.
3. Large volumes of regeneration waste are generated.
4. Although fluoride is highly preferred by activated alumina, some less preferred ions may compete strongly if present in large quantities.

5. The highly specific interaction of activated alumina with some species (e.g. arsenic, silica) may make regeneration difficult.
6. Many operational, control and maintenance problems have been encountered in the field, including clogging (especially when alum is used as a regenerant) and cementing of the bed.

3.2.6 Anion Exchange Resins

Ion exchange and adsorption principles are used interchangeably throughout the literature to describe the fluoride removal mechanism of activated alumina and bone materials. A combination of the two processes is thought to be probable. Some materials, however, are purely ion exchangers which release either positive or negative ions that have been held electrostatically on the surface, in exchange for ions of like charge from the solution the exchanger is in contact with. It is a reversible interchange between ions, so the exchanger can be regenerated by a concentrated solution containing the exchangeable ion.

Ion exchange processes occur naturally in soils, minerals, etc. The discovery of natural zeolite (hydrous silicates of aluminum and sodium) as a practical ion exchange material led to the development of synthetic zeolite. Boruff (1934) found limited capacity of this material in removing fluorides. A number of early patented ion exchange materials were also reported by Maier (1947, 1953), all showing some capacity for fluoride removal. Synthetic resins are presently used for most ion exchange applications. Through advanced resin development, a wide spectrum of synthetic resins have been introduced for various applications. Within the category of either cation or anion exchangers, many resins are tailored to selectively remove one ionic species over the others. For fluoride removal, an anion exchange resin would be appropriate. Anion exchange resins can remove fluoride by as much as 95 % before breakthrough occurs (Watson *et al.* 1974). Unfortunately, none of the commercially available resins of this type shows sufficient specificity for fluoride ion to allow practical use as a fluoride exchanger in the presence of other anions.

In the pH range of 6.5 to 8.5 and in dilute waters ($<$ 700 mg/L total dissolved solids), strong-base anion exchange resins prefer ions in the following order (Clifford 1982):

$$SO_4^{2-} >> NO_3^- >> Cl^- > HCO_3^- >> F^-$$

The magnitude of the separation factors of one ion over another depends on the resin chosen

but all commercially available anion exchange resins generally follow this selectivity sequence. In the exchange column, a more preferred species displaces a less preferred species which then retreats towards the outlet of the column, and chromatographic separation of anions in distinct zones are set up in accordance to the preference series. These zones move towards the outlet and obviously the breakthrough first occurs for the least preferred species. Except for the most preferred species, the breakthrough point of any ion of interest must be anticipated and not exceeded, because once breakthrough occurs, the effluent concentration of that ion will be greater than the influent concentration as the ion is being displaced out of the column. The breakthrough is abrupt rather than gradual as compared to activated alumina because of the kinetically superior behaviour of resins.

Since practically all major anions are preferred over fluoride, the fluoride capacity of anion resins depends on the F^-/total anions ratio. Capacities of synthetic resins are reported to be 2 to 4 meq/g as compared to 0.6 meq/g in the case of activated alumina (Rigdon 1980). If fluoride was the only aqueous species, capacities of synthetic anion exchange resins for this ion would be excellent. Unfortunately, the F^-/total anions ratios in natural waters are usually very low. Thompson and McGarvey (1953) investigated the use of a strong-base anion exchange resin in the chloride form for fluoride removal. The fluoride exchange capacity versus the F^-/total anions ratio is plotted in Figure 22. If this resin had been used to treat the Bartlett water which had a F^-/total anions ratio of 0.0147 (Maier 1953), the fluoride capacity would have been only 17 g/m^3.

The capital cost of an ion exchange resin system is similar to that of an activated alumina system of comparable size except that synthetic resins cost 10 times as much as activated alumina (Sorg 1982). Because of their relatively low fluoride capacities, synthetic anion resins are generally not economical for use in fluoride removal. However, synthetic anion resins were given serious consideration by Rigdon (1980) to treat a geothermal water in which F^- and HCO_3 made up 80 % of the anions. The water was of good quality (200 to 300 mg/L total dissolved solids) except for fluoride (15 to 25 mg/L). Thompson and McGravey (1953) reported on the preliminary laboratory work in fluoride removal for a food packing plant installation using Amberlite XE-98 resin and concluded that adequate quantites of water could be treated when only small amounts of fluoride needed removal. The resin, when regenerated with 40 kg NaCl per m^3 resin, had the capacity to treat 134,000 L/m^3 while removing 0.8 mg/L

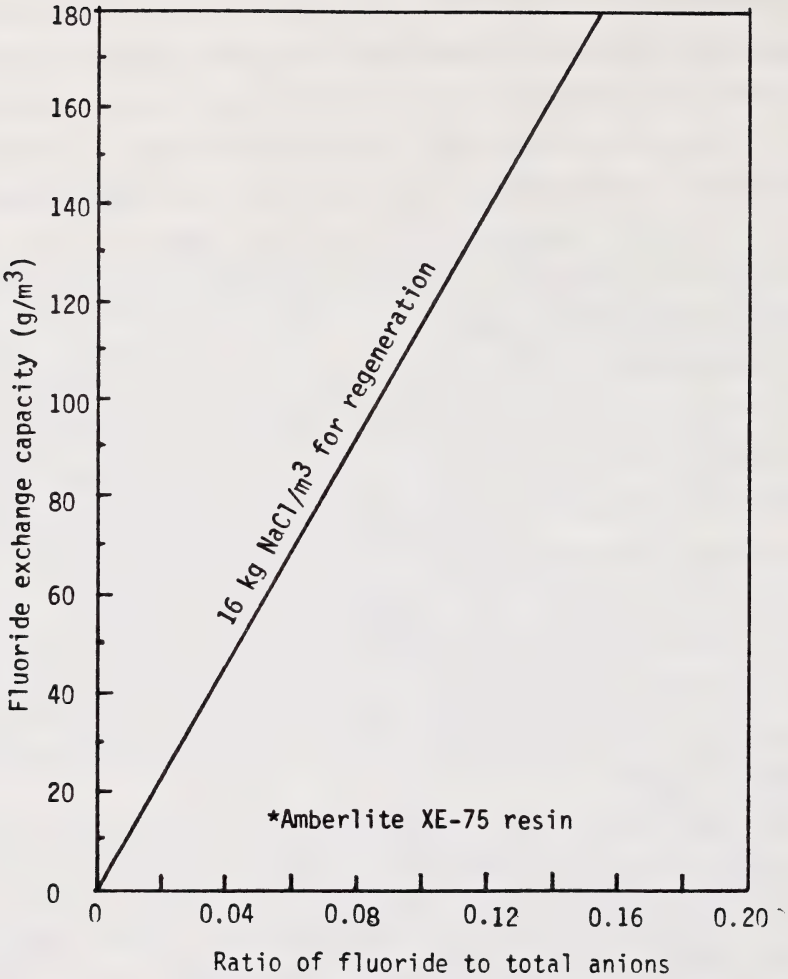


Figure 22. Fluoride capacity of a strong-base anion exchange resin (Thompson and McGravey 1953)

fluoride. The F^-/total anions ratio was 0.0417. Synthetic anion resins may also be practical when other anions need to be removed along with fluoride providing the fluoride capacity is not exceeded while removing the other ions. A mixed-bed (cation and anion resins) ion exchanger was used at one installation in Southern California (Harmon and Kalichman 1965) to demineralize high-fluoride water.

There has been extensive large-scale experience with ion exchange systems for softening, nitrate removal and demineralization. The feed water must be free of suspended solids and dissolved organics, which can lower the resin's exchange capacity. Clifford (1982) reported on some general design criteria. Typical package-type (190 to 760 L/min) resin beds were reported 1 to 2 m deep by 0.6 to 1.5 m diameter, and to contain 20 to 50 mesh material. Typical loading and regeneration flow rates were 2 to 10 L/s/m^3 and 0.5 to 1.0 L/s/m^3, respectively. Minimum regenerant contact time was 45 minutes. Near stoichiometrical regeneration is now possible for many commercial resins. Advanced regeneration techniques such as continuous or pulsed flow are employed in some plants. Continuous regeneration is efficient for large plants. As compared to batch regeneration, it results in greater removal efficiency, less media, more uniform product quality and more efficient use of chemicals. Like all column methods, the labour and chemical costs of regeneration make up a major expense of treatment. The toxic spent regenerant (4 to 10 % of product flow, Clifford 1982), must be safely disposed of.

3.2.7 Other Media

A variety of adsorbents used in contact beds have been reported in the early literature for possible fluoride removal. These include bauxite and silica gel (Boruff 1934); activated carbon (McKee and Johnston 1934); as well as insoluble aluminum compounds and hydrated metallic oxides other than alumina (Maier 1947). The methods using aluminum compounds involved soaking insoluble materials (e.g. sand, zeolites, natural adsorbents) in aluminum salt solutions, or reacting either sodium silicate; barium chloride; sodium phosphate; ferrous sulphate or titanium chloride with excess aluminum to form an insoluble compound. All these materials were found either ineffective or impractical by these early investigations. None of these has been demonstrated on a plant-scale basis. With the possible exceptions of activated carbon and bauxite, there is seemingly no current interest in further studying these materials

for fluoride removal. Bauxite in the activated form showed promise when studied by Choi and Chen (1979).

The use of carbon for fluoride removal was first investigated by McKee and Johnston (1934) who found that the activated form was effective but only when pH had been reduced to below 3.0. Near complete removal was possible at a low enough pH. This has been confirmed by Sollo *et al.* (1978) in jar tests. This pH limitation would probably be too costly for plant operation. Activated carbon was again studied by Choi and Chen (1979) as a comparison to activated alumina and activated bauxite based on batch adsorption of fluorides. Activated carbon was distinctly inferior to the other two in all aspects. However, certain types of activated carbon, probably those with high metallic impurities, may be sufficiently effective if the water is low in salinity and fluoride content. Activated bauxite performed very much like activated alumina, showing qualities of an excellent adsorbent for fluorides. In general, activated bauxite was out-performed by activated alumina but the bauxite was said to be a cheaper material.

3.3 DEMINERALIZATION METHODS

3.3.1 General

Demineralization processes are non-selective processes reducing all dissolved inorganics and yielding high overall quality of water. They are applicable to the treatment of brackish waters, high in total dissolved solids (TDS) - more than 1,000 mg/L; or in the situation where a combination of processes would otherwise be needed to remove a number of contaminants. Fluoride removal may be economically and efficiently accommodated in the demineralization process under these special circumstances.

For deionizing small flows of brackish water in municipal-scale water treatment, reverse osmosis and electrodialysis are the methods of choice. These are relatively new processes and they are similar in that they both use semi-permeable membranes to separate dissolved ions from the finished water. Both processes are energy intensive and produce high volumes of concentrated waste brines (20 to 50 % of product flow, Clifford 1982). The brines may not be as toxic as the regenerant wastes from adsorption or ion exchange columns although the quantities are substantially greater. The flows and concentrations of the feed, product and

waste are related to one another as follows:

$$Cb / Cf = Xs / Xw \quad (11)$$

$$Xs = 1 - (Qp\ Cp / Qf\ Cf) \quad (12)$$

$$Xw = 1 - (Qp / Qf) \quad (13)$$

where,

Cb = solute concentration of waste

Cf = solute concentration of feed

Cp = solute concentration of product

Qf = feed flow

Qp = product flow

Xs = fraction solute wasted

Xw = fraction water wasted

The term Qp / Qf is referred to as recovery.

3.3.2 Reverse Osmosis

3.3.2.1 Principle and System Design

Semi-permeable membranes allow passage of water molecules but reject most dissolved ions and some nonionic species. When a semi-permeable membrane separates a concentrated solution from a dilute solution, the osmotic pressure differential between the two solutions forces a net migration of water from the dilute side to the concentrated side of the membrane. Reverse osmosis (RO) is a reversal of this process, accomplished by applying a pressure on the concentrated side in excess of the opposing osmotic pressure, thereby concentrating brine on one side and producing deionized water on the other. The water passage, Qp (volume/time), and solute passage, Qs (mass/time) are expressed in the following equations:

$$Qp = Wp\ A\ (\Delta P - \Delta \pi^{\circ}) \quad (14)$$

$$Qs = Kp\ A\ \Delta C \quad (15)$$

where,

Wp = coefficient of water permeation

Kp = coefficient of solute permeability

A = surface area of membrane

ΔP = feed pressure

$\Delta\pi^{\circ}$ = osmotic pressure differential across the membrane

ΔC = solute concentration gradient across the membrane

$\Delta\pi^{\circ}$ is a function of ΔC and, as a rule of thumb, can be taken as 70 kPa per 1,000 mg/L TDS for natural waters. Wp and Kp are characteristic of the membrane. It can be shown from the equations that the product flow and quality decrease with decreased driving pressure, increased feed concentration, or increased recovery.

The rejection efficiency for individual species is related to the size and charge of the species. The small monovalent F^- is not as effectively removed as the larger monovalent HCO_3^- or divalent SO_4^{2-} for instance. Co-ions also affect the rejection of counter-ions. F^- would be better rejected as CaF_2 than as NaF since the divalent Ca^{2+} is better rejected than the monovalent Na^+.

RO membrane modules are available in several designs. The tubular design has a rather large flow channel and is less susceptible to clogging. The other types are hollow fine fiber and spiral wound designs. These modules require extensive pretreatment such as turbidity reduction to less than 1.0 JTU (Watson *et al.* 1974). A reverse osmosis system consists of a series-parallel arrangement of modules. The parallel arrangement allows a sufficient quantity of the total product flow. The series arrangement increases the overall product recovery and/or removal efficiency of the system.

3.3.2.2 Performance and Operating Conditions

Maximum fluoride removal efficiency of the RO process is generally reported to be 90 to 97 % (O'Brien 1983; Watson *et al.* 1974). The actual performance of a RO system in removing any contaminant is dependent on the feed concentration of the contaminant, the recovery ratio, pH of the system, the efficiency of the membrane material, the operating pressure, and the adequacy of pretreatment to remove or inhibit the formation of detrimental substances. The optimum recovery ratio is selected to produce water of sufficient quality while maintaining an adequate product flow. Individual membrane modules normally operate at 30 to 50 % recovery to maintain a sufficient brine flow that will minimize scaling and fouling problems (Clifford 1982). Modules are staged on the brine side to achieve higher overall recoveries, an arrangement similar to the staging of product flow for increased removal efficiencies. Typical overall recovery is 75 %. Fluoride removal is highly pH dependent with sharp decreases below pH 6.0 (Clifford 1982). A reverse osmosis manufacturer (DuPont, cited

by Sorg 1978) reports that fluoride removal increases from 45 to 90 % as the pH increases from 5.5 to 7.0. Commercially available membranes are commonly a cellulose acetate material. The membrane flux of this material is reported to be 34 to 56 L/m²/d, at 2,700 to 4,000 kPa operating pressures (Watson *et al.* 1974). This flux tends to decline logarithmically with time. Periodical cleaning can only partially restore the flux. Permanent decline due to pressure compaction of the membrane material will eventually lead to the need for membrane replacement.

There are two standard pressure systems. As reported by Huxstep (1981), the high pressure system, operating at 2,800 kPa, has high flow capacity and treatment efficiency. It is applicable to brackish waters containing 1,000 to 15,000 mg/L TDS and is effective in reducing the TDS to less than 500 mg/L. The low pressure system, operating at 1,400 kPa, is comparatively inferior in performance but recent development of low pressure membranes has improved contaminant removals to as high as 80 to 90 %. The low pressure system has a lower energy requirement and is economical for small flows or where high removals are not required. Huxstep conducted pilot work to investigate performance of the two systems in removal of a number of contaminants including fluoride. Both systems used spiral-wound cellulose acetate membranes, operated at 75 % recovery and were double-staged. For various practical reasons, pressures somewhat lower than the standards were used during the investigation. The high pressure system out-performed the low pressure system significantly in terms of higher removal of all contaminants. The order of rejection, based on the relative percentage removal values of different contaminants, was almost the same for both systems. The low pressure system had a much wider range of percentage removal values. The results of fluoride removal are presented in Table 7. At four influent fluoride levels from 4.7 to 12.6 mg/L, the removal efficiencies were consistently about 90 % for the high pressure system and 60 % for the low pressure system. Based on these data and an allowable fluoride concentration of 1.5 mg/L in the effluent, the high pressure system could treat water containing as high as 15 mg/L F^- while for the low pressure system, 3.8 mg/L would be the maximum influent F^- limit. The highly efficient high pressure system would provide the opportunity for blending raw and treated waters.

Successful operation of the RO system relies on proper pretreatment to prevent scaling, fouling, plugging and biological growths. The pH must be kept below 9.0 in order to prevent hydrolysis of the membrane. $CaCO_3$ and $CaSO_4$ scales are controlled by lowering pH to below

Table 7. Fluoride removal by reverse osmosis

(Huxstep 1981)

Test Period Days of Operation	Source Water Concentration (mg/L)	HIGH PRESSURE SYSTEM			LOW PRESSURE SYSTEM		
		Product (mg/L)	Reject (mg/L)	Percent Removal	Product (mg/L)	Reject (mg/L)	Percent Removal
1 - 5	4.72	0.31	14.08	93.4	1.86	13.99	60.6
6	7.06	0.60	21.85	91.5	2.97	22.55	57.9
7 - 8	8.84	0.86	27.10	90.3	3.69	27.38	58.3
9 - 10	12.56	0.94	37.36	92.5	4.72	37.88	62.4

6.5 and/or by sequesterant addition. Fouling is controlled by granular bed filtration to remove iron or manganese precipitates, organics and clays. These substances may also be eliminated by oxidation and/or polyelectrolyte addition. Particulate plugging is prevented by cartridge filtration immediately ahead of the membrane modules. Chlorination is used to control bacterial growths in cellulose acetate modules. A chlorination/dechlorination sequence or ultraviolet irradiation is used for aramid membranes (Clifford 1982) which cannot withstand chlorine attack.

3.3.2.3 Costs

RO treatment generally costs considerably more than processes that involve single-contaminant removal. Therefore the process is practical only when a number of contaminants need to be removed or lowering of the TDS is required. Figure 23, developed by Gumerman *et al.* (1979, cited by Sorg 1980), shows that the construction cost escalates rapidly with increasing plant size. Comparing this figure with Figure 20, a 1.0 ML/d RO plant would cost 4 times more than an activated alumina plant of the same capacity. The construction cost of a RO plant may vary considerably depending on the pretreatment and post-treatment equipment involved. The costs plotted in Figure 23 were likely to be on the low side for 1979 prices as they seem to be comparable to earlier costs - those reported by Sorg *et al.* (1980) for plants constructed between 1974 and 1976, and those estimated by the U.S. Department of the Interior (1972, cited by Watson *et al.* 1974) at 1973 prices (Figure 27).

Operating cost items include power, membrane replacement, labour, etc. Pretreatment and post-treatment costs, brine disposal cost and savings in blending waters would be highly site specific. Power requirements for the RO process are high, typically 2,640 kW·h/kL product (Watson *et al.* 1974). Figure 24 compares this energy on a daily requirement basis with that estimated for ion exchange plants (U.S. Department of the Interior 1972, cited by Watson *et al.* 1974). Membrane replacement cost is also a substantial portion of the operating cost. It can amount to as high as 30 to 40 % of the total operating cost. Figure 25 shows the operating cost curve developed by Gumerman *et al.* (1979, cited by Sorg 1980). This shows RO to be more costly than the activated alumina process when compared with the activated alumina curve developed by the same workers in Figure 21.

Rigdon (1980) reviewed the cost data of several RO plants. The unit treatment costs of seven plants reported by Hornbury *et al.* (1976, cited by Rigdon 1980) were $0.14 to 0.33/kL

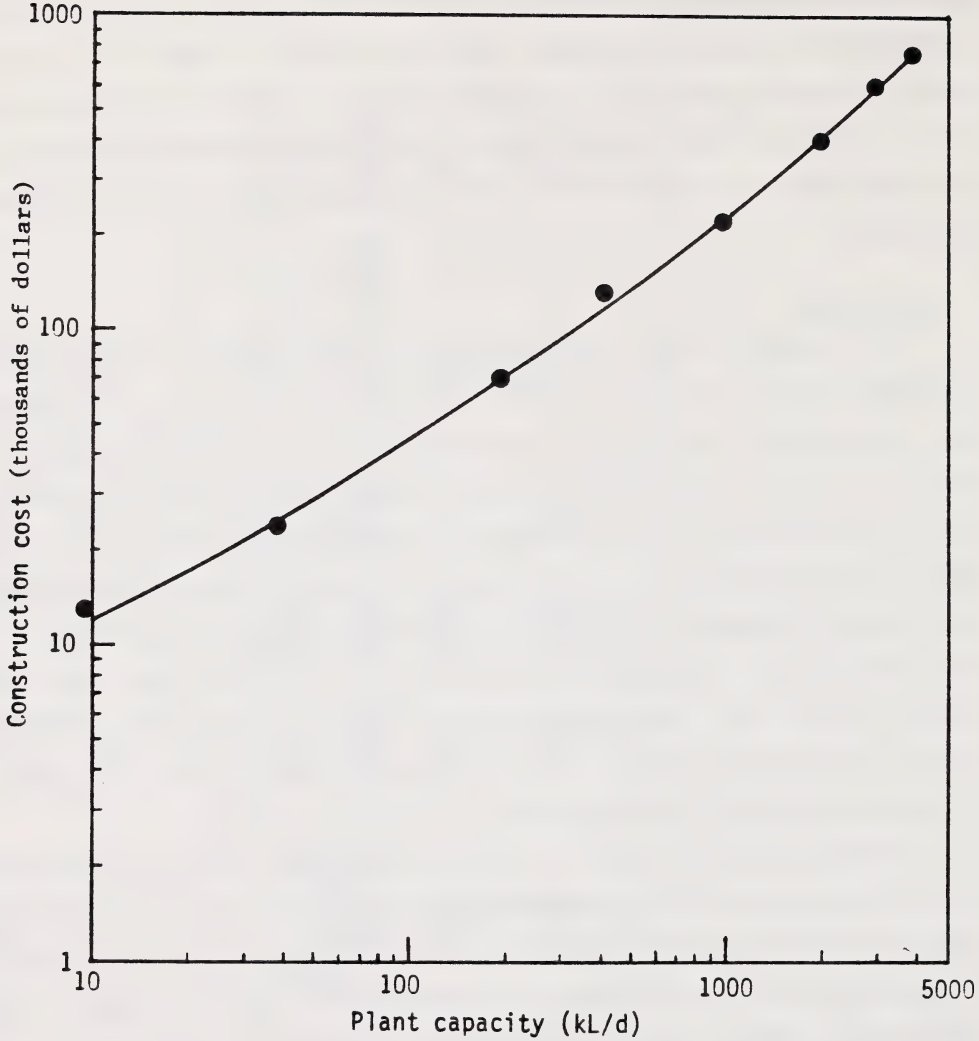
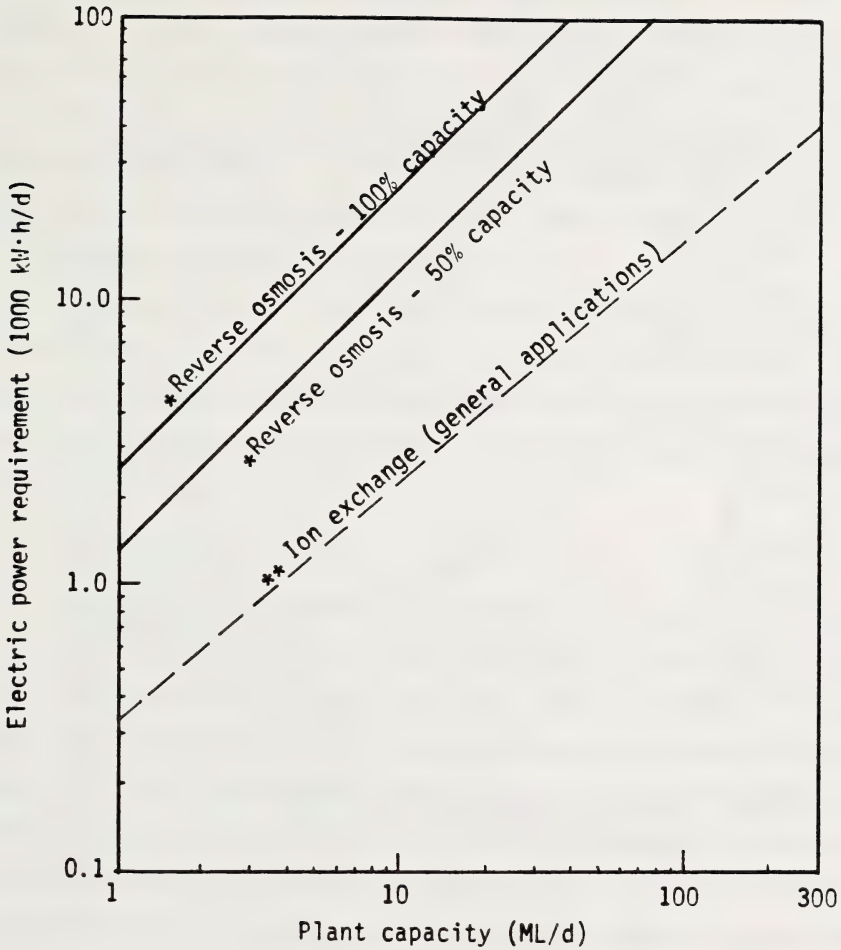


Figure 23. Construction cost for reverse osmosis plants

(source: Sorg 1980, after Gumerman *et al.* 1979)



* Reverse osmosis curves derived from Watson et al. 1974

** Ion exchange curve after U.S. Dept. of the Interior 1972, source: Watson et al. 1974

Figure 24. Energy requirements for reverse osmosis plants

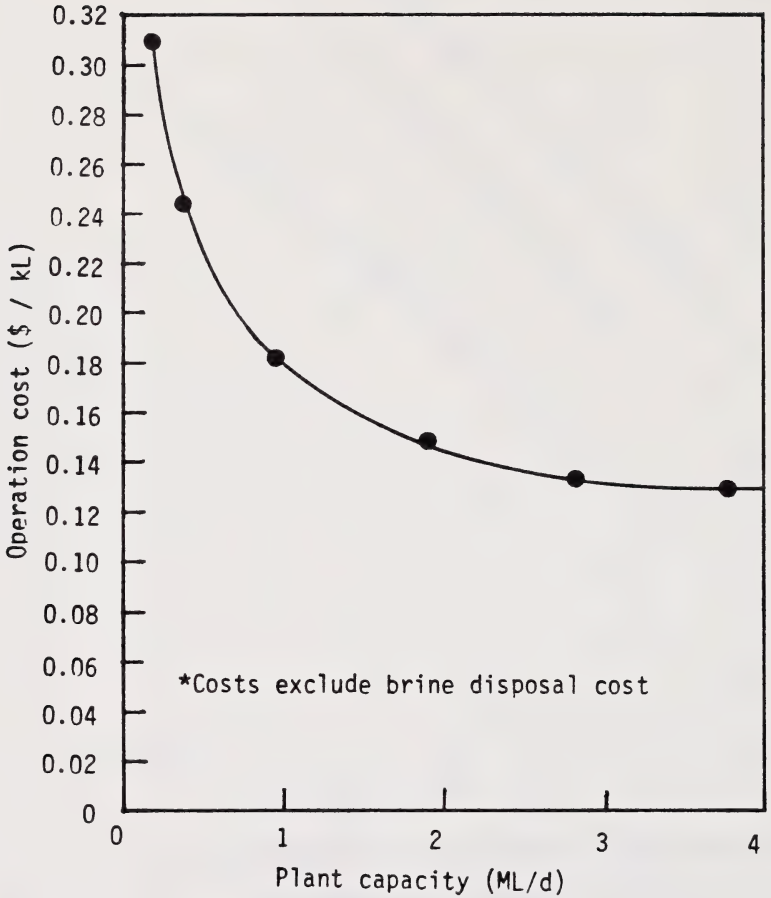


Figure 25. Operation cost for reverse osmosis plants
(source: Sorg 1980, after Gumerman *et al.* 1979)

(presumably including capital amortization) during the 1970 to 1975 period. The plants operated at 0.009 to 3.5 ML/d capacities, treating 1,500 to 7,000 mg/L TDS. Another plant (Moore 1972, cited by Rigdon 1980) treated water at $0.20/kL which included amortized capital. This plant had a design capacity of 0.57 ML/d, operated at 54 % capacity and reduced TDS from 2,250 to 500 mg/L. In 1979 dollars, Rigdon estimated costs of RO treatment for the geothermal water studied (980 ML annual product volume) at $0.20 to 0.30 per L/d capacity for capital investment and $0.15 to 0.18/kL for operation.

Additional cost data of eight RO systems in Sarasota County, Florida have been reported by Sorg *et al.* (1980). These will be presented with the case studies in the next section. From the most recent estimates by O'Brien (1983), based upon capital amortized on a 20-year term at 12 %, the RO treatment cost was about $0.80/kL for a plant size in the range of 1.0 to 5.5 ML/d (Figure 30).

3.3.2.4 Case Studies

Sorg *et al.* (1980) reported on eight RO systems in Sarasota County, Florida. These systems had been built primarily for radium-226 removal but three of the water supplies also had fluoride concentrations in the 2.0 to 2.2 mg/L range. The majority of these installations were small systems treating well water for mobile homes. The design capacities ranged from 0.003 to 3.8 ML/d. The two smallest systems operated at a 1,400 kPa pressure while the rest operated at 2,800 to 2,900 kPa. All systems used either hollow fiber or spiral wound type of membrane modules. Fluoride removals ranged from 57 % to 85 %. Surprisingly, the highest and third highest (75 %) removals were reported at the low pressure systems. However, the difference in design, operation and age of the membranes of the individual systems must be thoroughly considered in order to make a fair comparison.

Pretreatment for these systems included cartridge filtration, pH adjustment to about 6.0, calcium and magnesium sequestration with sodium hexametaphosphate, and iron removal by ion exchange. Post-treatment generally consisted of pH adjustment, H_2S degasification and chlorination. Some membrane failure problems due to fouling were experienced in most installations. Some smaller systems operated only sporadically during the off-peak season (summer months for trailer parks) and bacterial fouling occasionally developed because of low flows. Other maintenance problems included corrosion from hydrogen sulfide gas and sulfuric acid, noise, vibration, and high pressure pump failures. Although the reject waters were highly

concentrated, the quantities were relatively small for small installations. Disposal methods involved discharge to a tile field, to surface waters, to storm sewers or to a holding pond.

The estimated operating costs (1977) ranged from $0.16/kL (for the largest system)to $0.41/kL. These cost estimates included chemical, power ($0.04/kW·h), filter cartridge replacement and labour costs; but excluded membrane replacement and amortization costs and savings in blending waters.

3.3.2.5 Advantages

1. RO treatment produces a water of excellent overall quality along with relatively high fluoride removal. The treated water is soft, palatable and non-corrosive.
2. The high quality of product water provides the opportunity of blending with raw water.
3. The system has small space requirement; package plants are available.
4. A continuous flow of reject water may be easier to handle than the slugs of regenerant or sludge wastes. The reject water is usually less toxic than the regenerant waste.
5. The RO process is practical for high TDS waters. It does not have the problem of one substance interfering with the removal of another.
6. The method can be successfully used to treat small water supplies.

3.3.2.6 Disadvantages

1. The RO process is not designed specifically for fluoride removal and practical application of this method is limited to high TDS waters.
2. The degree of blending the raw and treated waters to meet the objective fluoride level may not satisfy the quality of water in other respects (e.g. TDS).
3. It has a high operation cost because of high energy consumption. Economies of scales apply for larger systems.
4. There is the problem of disposing large quantities of reject water, although other treatment methods also have similar problems.
5. RO membranes are susceptible to scaling, fouling, plugging and bacterial attack. Extensive pretreatment may be required.
6. The membranes can also be damaged by high pressures or by freezing.

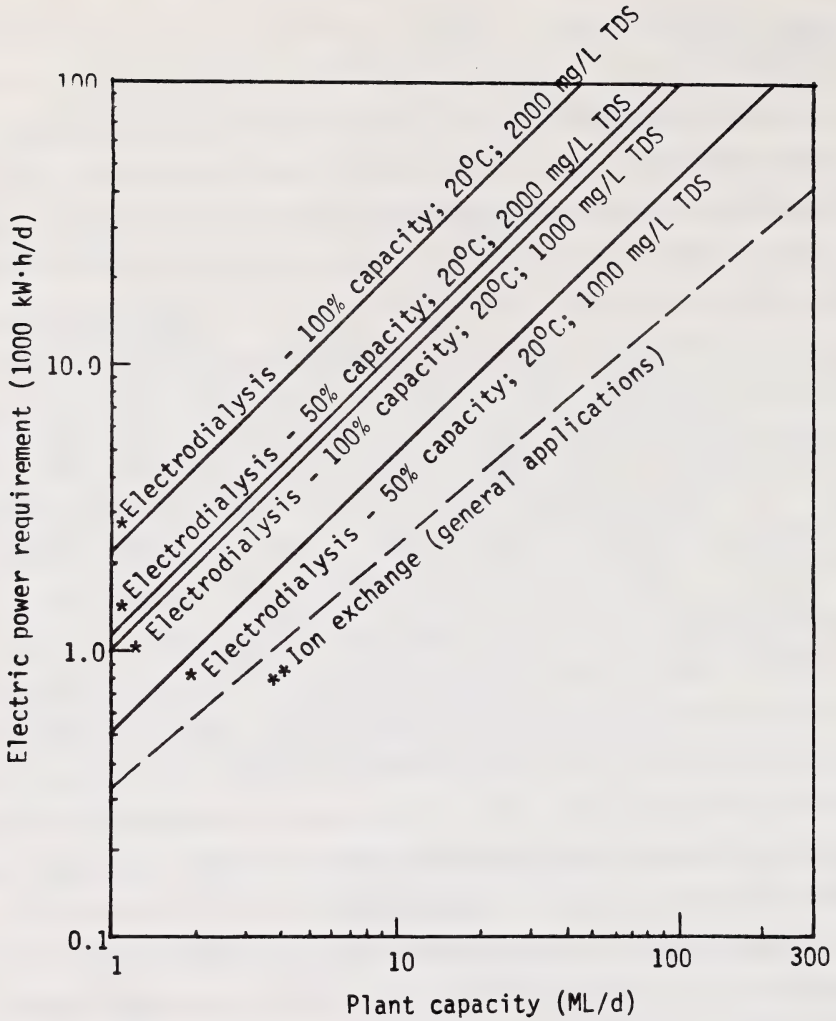
3.3.3 Electrodialysis

In the electrodialysis (ED) process, work is done to move ions rather than water. A D.C. electric current transports cations in one direction and anions in the opposite direction. Alternate layers of cation- and anion-permeable membranes perpendicular to the current path, each permitting passage of one type of ions while rejecting the other, establish alternate ion-depleting and ion-concentrating cells. Water is fed between the membrane pairs at one end while brine and product waters are drawn at the other end from the ion-concentrating and ion-depleting cells, respectively. A stack is made up of a number of cell pairs between the end cathode and anode compartments where the voltage is generated. There is a maximum flow rate per stack, and stacks are set up in parallel to produce increasing flow rates. Two or more sets of parallel stacks may be arranged in stages to increase removals. TDS removal per stage is 30 to 50 % (Watson *et al.* 1974). Calculations for the determination of the required number of stacks and stages were detailed in Watson *et al.*'s report based on TDS removal.

Fluoride removal by the ED process has been reported to be 80 % efficient (O'Brien 1983; Watson *et al.* 1974). Accordingly, for a residual limit of 1.5 mg/L, the maximum fluoride concentration in the feed is 7.5 mg/L. Other available performance data are generally limited to TDS removal which is the design basis for the process. TDS removal is a function of temperature, the amounts and kinds of dissolved solids, flow rate and stack design. Generally, the product water quality is lower for ED than for RO.

An ED system operates at about the same recovery range (40 to 80 %) as a RO system and generates comparative amounts of waste flow. The energy requirement depends on TDS and is proportional to the electrical equivalents of salts. Because it is the ions that are moved rather than water, the energy requirement for ED (Figure 26) is somewhat lower as compared to the RO system (Figure 24). Pretreatment requirements are similar to those for the RO process. However, ED membranes are less susceptible to scaling, fouling, plugging and are immune to biological attack; and therefore require less pretreatment. A recent revolutionary development involves a reversal of the current flow for self-cleaning. In the ED process, oxygen and chlorine produced at the anode and hydrogen produced at the cathode are vented to the atmosphere.

Treatment costs of ED plants are expected to compare closely with those of RO plants. Similarly, ED plants are built for TDS reduction and with the expectation of several removal



* Electrodialysis curves derived from Watson et al. 1974

** Ion exchange curve after U.S. Dept. of the Interior 1972, source: Watson et al. 1974

Figure 26. Energy requirements for electrodialysis plants

parameters sharing the total cost of treatment. On the basis of operating data between 1963 and 1970 for an ED plant (2.5 ML/d capacity) which was reducing 1,500 to 2,500 mg/L TDS to 500 mg/L, Scheffer (1972, cited by Rigdon 1980) estimated the average operating costs for 30 % and 90 % loading factors at $0.19/kL and $0.11/kL, respectively. An additional $0.05 to $0.15/kL would be for capital amortization and cost of blowdown water. Several plants at 0.26 to 7.6 ML/d capacities (Hornburg *et al.* 1976, cited by Rigdon 1980) reported average treatment costs (1970 to 1975) at $0.14 to $0.33/kL, including amortized capital. Rigdon (1980) estimated the capital and operating costs of ED for treating a particular water at $0.22 to $0.24 per L/d capacity and $0.11 to $0.17/kL, respectively (1979 dollars). Recent estimates by O'Brien (1983) indicated that ED treatment cost varied from $0.55/kL for a 6 ML/d plant size to $0.75/kL for a 1 ML/d plant size (Figure 30). These were based upon capital amortized on a 20-year life at 12 % interest.

The ED process shares many of the advantages and disadvantages with RO. As far as the overall quality of the treated water is concerned, ED is generally inferior to RO. It can only remove ionic species and fails to remove large organic ions or colloids.

4. SUMMARY COMPARISON

High fluoride content in groundwater presents a serious problem to many small communities which rely on such sources for water supply. A defluoridation process is feasible for small communities only if it is comparable to conventional treatment processes in cost, equipment and simplicity of operation.

The additive methods involve conventional coagulation or softening processes and are particularly suitable when a treatment plant which includes such processes already exists, or is otherwise needed. In such cases, fluoride removal can be readily incorporated by simple modifications. Because of high capital cost, constructing such a plant solely for fluoride removal or for home application is not practical. In any event, these methods are generally limited to waters containing relatively low levels of fluoride (< 3.0 mg/L). Otherwise, excessive chemical requirements and high production of sludge would escalate the operating cost to an impractical level.

Reverse osmosis and electrodialysis are relatively new treatment processes and have not been researched adequately or demonstrated on a full-scale basis specifically for fluoride removal. In spite of high energy costs, these processes are effective and may be practical for treating small community water supplies when the total dissolved solids are high.

Processes using contact columns appear to be most reliable for specific fluoride removal and can be operated on demand. Column methods are most effective at 5 to 10 mg/L fluoride (Sollo *et al.* 1978) although they have been used at lower concentrations. The unit may be designed for all sizes of installation down to the household size, similar to a commercial water softener. Anion exchange resins are not preferred for fluoride removal because of their low selectivity for this ion and the effectiveness depends on the F^-/total anions ratio. However, there have been many years of experience using bone materials and activated alumina in defluoridation columns. Maier (1953, 1960, 1971), who reported most of the past plant experience with these materials, found that these plants were comparable to softening (ion exchange) plants in cost, equipment, operation and degree of maintenance, and that waterworks employees could become operators after adequate training. Nevertheless, the literature generally indicates that the successful use of bone materials or alumina relies heavily on careful control and handling of reagents, making these processes fairly complicated. Likewise, waste disposal is potentially a major problem.

Among the bone materials tried, bone char has been demonstrated most successful in full-scale operations. This material has also been suggested for small installations and for home application on a throw-away basis. All bone materials tend to distinegrate (by attrition and by acid) and lose capacity to some extent when the same bed is used continuously. Activated alumina is presently the preferred and the cheapest material to be used in municipal plants. When the optimum process environment is carefully maintained, it is superior to bone char in performance. The stringent requirments for pH control make the activated alumina process difficult for home application even when the exhausted bed is not regenerated.

Treatment costs are highly site-specific. Moreover, cost estimates given by the literature in most cases are ambiguous to a certain extent as the exact cost items included in the calculations are not always clear. Therefore, the cost data presented in this general review are intended only to provide a comparison among individual processes. In order to make a fair comparison among individual processes, additional comparison charts are given in Figures 27 to 30, each composed of specific data of different processes from the same reference source. For comparison purposes, the absolute dollar values are of little importance; some are obviously much out-of-date. The user of these charts must remember that only activated alumina and bone char facilities are constructed and operate entirely for fluoride removal, and therefore direct comparison of these systems with the other multi-purpose systems is not possible.

Before resorting to large-scale fluoride removal facilities, the possibility of an alternative water source, or at least blending such water with the existing water, should be considered. Unfortunately, a suitable water source is not always available in the vicinity. Depending on site-specific conditions of the community, there are still a number of possible treatment and water delivery arrangements that can satisfy the consumer without imposing an undue economic hardship. Where a plant already exists to treat water that requires softening, fluorides should be reduced as much as possible by the lime-softening process. Balancing the costs of pre-carbonation and sludge disposal against the addition of limited quantities of magnesium compounds and excess lime would be economical. The remaining fluorides can be reduced by contact filters or by alum coagulation. For highly efficient processes such as column adsorption, reverse osmosis or electrodialysis, raw and treated waters may be blended to produce savings while still satisfying the water quality standards. In the case of column adsorption, savings would be offset by the need for more frequent regeneration to maintain a

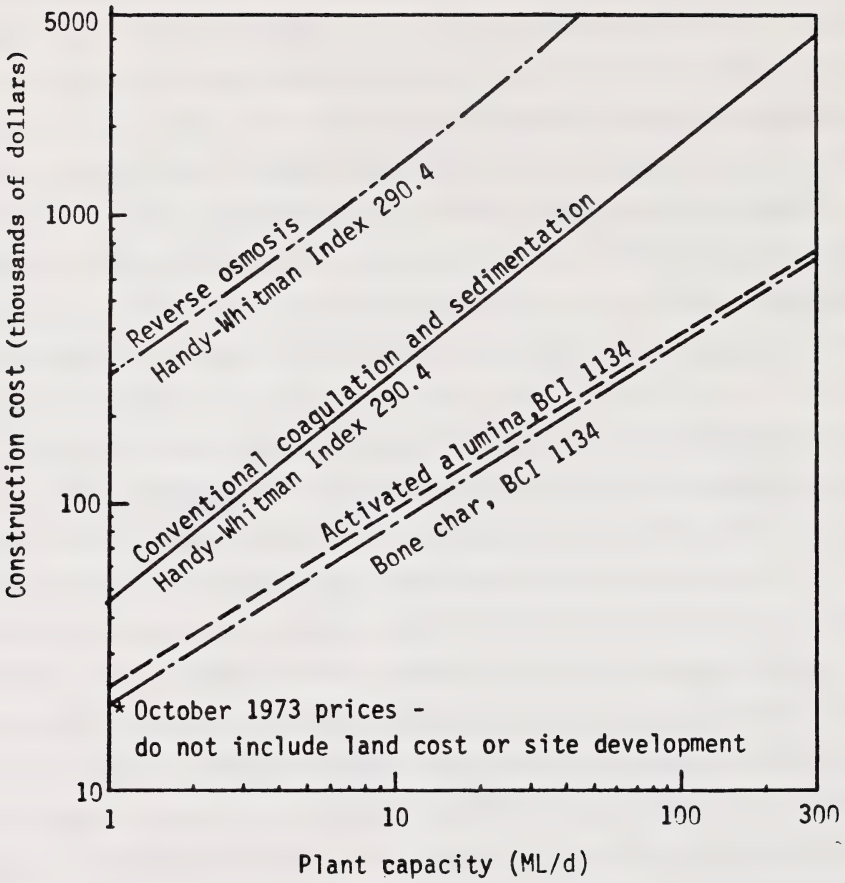


Figure 27. Construction cost comparison for different processes

Cost data from Watson *et al.* (1974)

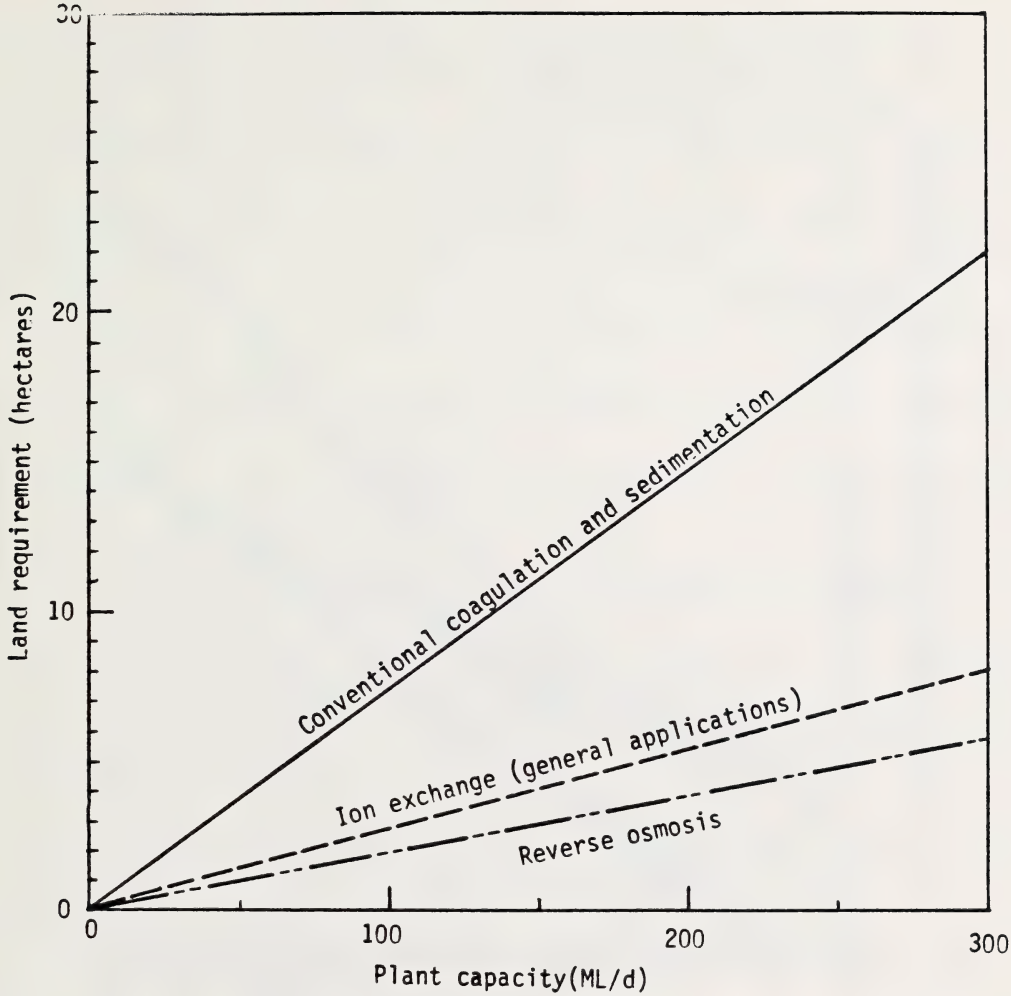


Figure 28. Land requirement comparison for different processes

Data from Watson *et al.* (1974)

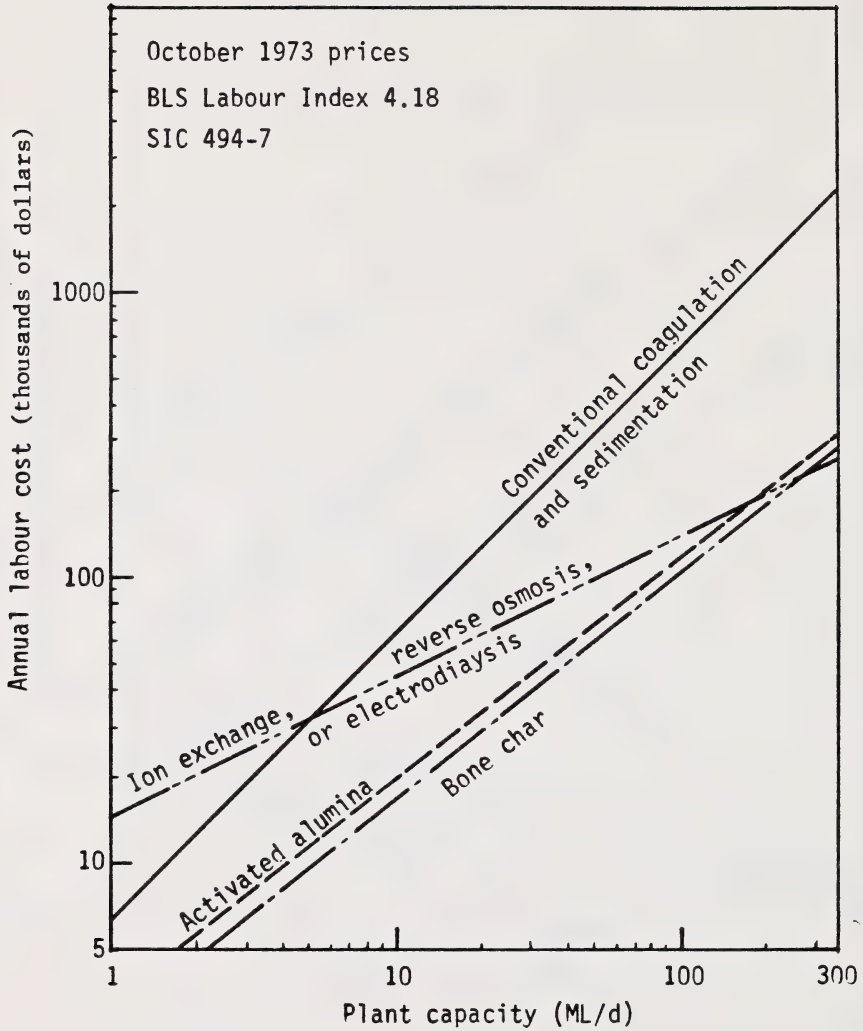
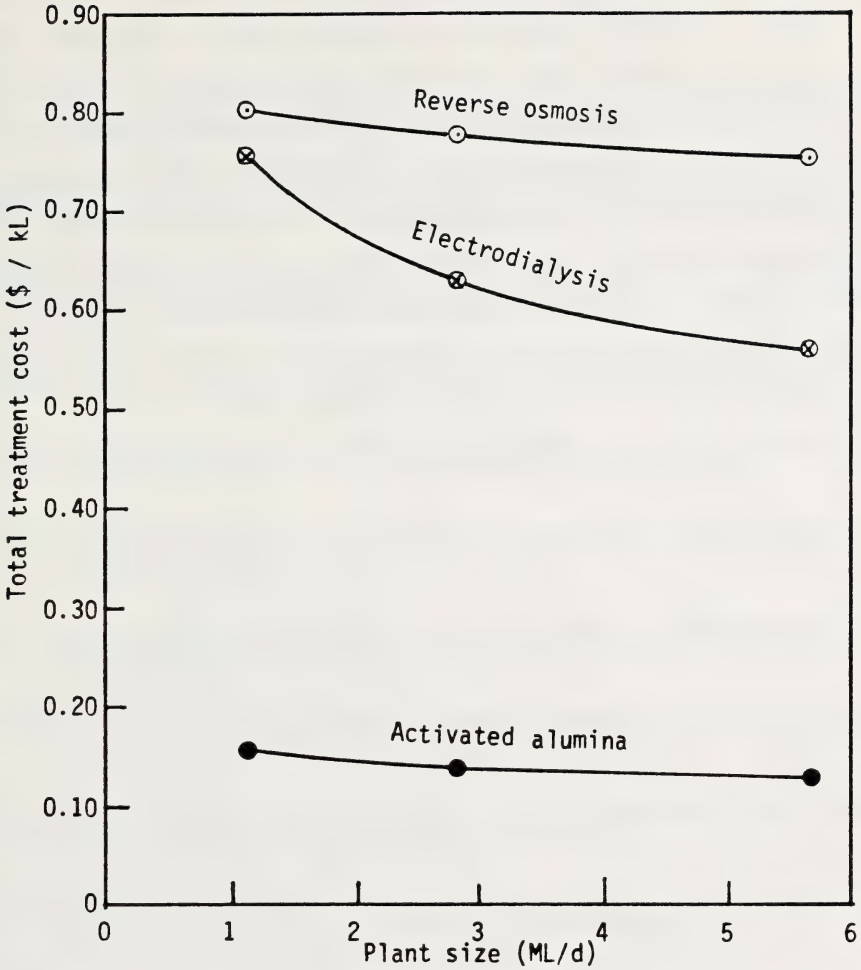


Figure 29. Labour cost comparison for different processes

Cost data from Watson *et al.* (1974)



*Based upon capital amortized on a 20-yr life @ 12% interest
Waste disposal not included

Figure 30. Total treatment cost comparison for different processes

Cost data for O'Brien (1983)

sufficiently low effluent fluoride concentration that allows blending.

Finally, management solutions may be applicable. Not all of the water in the water supply needs to be treated for fluoride reduction. If only enough water is treated for drinking and culinary purposes, the size of the treatment system could be substantially reduced. Depending on the most economical means for the community, defluoridated water may be made available to users by a separate piping system, by haul trucks, or in bottles. The separate piping system may deliver the water to individual residences, to centralized taps, or to drinking fountains in schools. Where low-fluoride water is not directly available at individual residences, a publicity program must be launched to promote public awareness of the high-fluoride problems and to ensure adequate use of the defluoridation system.

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